Proceedings

THE NINTH SYMPOSIUM
ON THE
ART OF GLASSBLOWING

1964

THE

AMERICAN SCIENTIFIC GLASSBLOWERS SOCIETY

Proceedings
THE NINTH SYMPOSIUM
ON THE
ART OF GLASSBLOWING

Sponsored by

THE AMERICAN SCIENTIFIC
GLASSBLOWERS SOCIETY

In Cooperation with

THE DELAWARE VALLEY SECTION
OF THE A.S.G.S.

SHERATON HOTEL
PHILADELPHIA, PENNSYLVANIA

MAY 25, 26, 27, 1964

Copyright 1964

THE AMERICAN SCIENTIFIC GLASSBLOWERS SOCIETY
309 Georgetown Avenue, Gwinhurst
Wilmington, Delaware 19809

FOREWORD

It is generally agreed by those responsible for the success of gatherings, such as this 9th Symposium and Exposition of The American Scientific Glassblowers Society, that some theme or slogan be adopted which points to the overall purpose of the meeting, and for this 9th Symposium it can be best described by one word, "PRACTICAL."

The Technical Papers Committee should be complimented in sensing this trend to practicality during past symposiums, and using it to select papers that contain information more applicable to the present demands on the research scientific glassblower.

Although this "PRACTICAL" theme, epitomized by the actual demonstrations in the "Art of Scientific Glassblowing," during the Work Shop Sessions, its application in the selection of the technical papers, resulted in a larger general attendance at all the technical meetings and also for the lively question and answer period following the conclusion of each paper.

As usual the technical papers were of high quality and on behalf of the 9th Symposium and Exposition Committee and of the Society, I want to officially thank the authors for their contribution to the success of the Symposium and to acknowledge in return their thanks for the special glass plaque with their name engraved thereon presented to each author at the conclusion of his paper. There is probably no activity of our Society that has contributed to the growth and general up-grading of the profession of Scientific Glassblowing than these yearly symposiums and the accompanying expositions. In presenting them the Scientific Glassblower has demonstrated beyond question his ability to plan and to execute a technical meeting of high professional quality, as well as his inherent ability to materialize in glass, the complex configurations for research, usually beyond the comprehension of the layman.

As this will perhaps be the last opportunity the writer will have the pleasure of contributing the "Foreword" to a set of "Proceedings" and before officially occupying the honored office of President Emeritus, I want to express my sincere appreciation and gratitude to those members who have through the years, shared my thoughts and desire to organize a technical society, whose aims, objectives and efforts would all be directed to the continued elevation of the profession of Scientific Glassblowing.

Most gratefully yours,

J. ALLEN ALEXANDER
President and Founder
The American Scientific Glassblowers Society

CONTENTS

OFFICERS AND DIRECTORS OF THE AMERICAN SCIENTIFIC GLASSBLOWERS SOCIETY FOR 1963 - 1964

OFFICERS

President—J. ALLEN ALEXANDER
Atlantic Refining Co., Philadelphia, Pa.

Vice-President—ALFRED H. WALROD
Varian Associates, Palo Alto, Calif.

Secretary—RICHARD A. KLEINERT
Bendix Corp., Detroit, Mich.

Treasurer—KARL H. WALTHER
Brookhaven National Lab., Upton, L. I., N. Y.

DIRECTORS-AT-LARGE

ARTHUR DOLENGA
General Motors Corp., Detroit, Mich.

HOWARD M. NUTT
The Linde Co., No. Tonawanda, N. Y.

RALPH H. RUSSLER
Johns Hopkins Univ., Baltimore, Md.

RANDOLPH H. SEARLE
E. I. du Pont Co. S.R.P., Aiken, S. C.

SECTIONAL DIRECTORS

CLAIR E. CAMPBELL—Great Lakes Section
JOHN A. GLOVER—Midwest Section
LEIGH B. HOWELL—Southern California Section
JOHN HYDRO, JR.—Washington-Baltimore Section
WILLIAM KRAVENKO—Pittsburgh Tri-State Area Section
DONALD E. LILLIE—Southeastern Section
MELVYN LOCKWOOD—San Francisco Bay Area Section
THOMAS J. MCKELVEY—Delaware Valley Section
IRVIN MEYER—Metropolitan New York Section
MATTHEW NAZZEWSKI—Hudson-Mohawk Valley Section
HOWARD M. NUTT—Niagara Frontier Section
ARTHUR G. REEVES—New England Section

EXECUTIVE SECRETARY

GEORGE A. SITES
Houdry Process & Chemical Co., Linwood, Pa.

HOME OFFICE

309 Georgetown Avenue
Gwinhurst
Wilmington, Delaware 19809

SYMPOSIUM COMMITTEE

General Chairman .... M. Howe Smith, Fischer & Porter Co.

Vice Chairman .... Helmut E. Drechsel, National Scientific Co.

Technical Papers . Dr. John H. Glaser, General Electric Co., Chairman

Workshops .... John F. Belz, Smith, Kline & French Labs., Chairman
Thomas J. McKelvey, Smith, Kline & French Labs., Vice Chairman

Publicity ..... James B. Lawrence, Bethlehem Apparatus Co., Chairman

Hospitality .... M. Howe Smith
Helmut E. Drechsel
J. Allen Alexander, Atlantic Refining Co.

Registration & Finance .... Thomas J. McKelvey, Chairman
Dolores I. Sites, A.S.G.S. Office Manager

Photography, Projection,
and Recording .... Walter P. Copeland, Gulf Oil Corp.
C. Donald Federline, Polytechnical Products Co.
Charles Bennett, Frankford Arsenal

Program Committee .... M. Howe Smith
Helmut E. Drechsel
James B. Lawrence

Glassware Display .... Joseph Bayard, The Fredericks Co.
Betty Bayard, The Fredericks Co.

Ladies Program .... Dorothy Drechsel, Chairlady
Jean Smith
Ada Alexander
Audrey Lawrence

Industrial Advisors .... Ronald Bolnick, Carlisle Gas Burner Co.
Columb Higgins, Fischer & Porter Co.
George Hahn, Woodland Ave. Machine Co.
James B. Lawrence, Bethlehem Apparatus Co., Inc.
Peter Davenport, Corning Glass Works
Arthur C. Peters, Owens-Illinois, Kimble

A.S.G.S. Advisors ..... George A. Sites, Houdry Process & Chemical Co.
J. Allen Alexander

Commercial Exhibits .... Helmut E. Drechsel, Chairman
Multi Service Associates, Phila., Pa., Managers

THE STRENGTH AND WEAKNESS OF BRITTLE MATERIALS

PROF. C. J. PHILLIPS
Rutgers University
New Brunswick, New Jersey

An abbreviation of a lecture given by Professor Phillips as national lecturer for the Society of the Sigma Xi.

Most methods of estimating the ultimate or theoretical cohesive strength of brittle solids agree that it should be of the order of several million pounds per square inch or more, and that it should be proportional to Young's modulus of elasticity. Unfortunately, strengths usually observed are seldom as much as 1 per cent of theoretical. This tremendous disparity can be explained, at least qualitatively, by the presence of surface flaws which act as stress concentrators.

There are several ways of increasing the ordinarily observed strength of brittle materials. These methods include fire polishing, chemical etching, ion exchange, tempering, and extreme care in handling. Under exceptional circumstances the effects of flaws can be so minimized that the observed strengths do then approach the theoretical limits. For example, glass fibers have been broken at stresses exceeding two million pounds per square inch.

Since most theoretical treatments of ultimate strength involve Young's modulus of elasticity, a study of that property as it relates to composition and structure should be illuminating. This kind of work has already led to the development of empirical factors which permit calculation of Young's modulus from composition of both simple and complex silicate glasses. Other data show a direct correlation between Young's modulus and modulus of rupture for both glasses and polycrystalline ceramic bodies.

ULTRAHIGH VACUUM TECHNOLOGY

RICHARD W. ROBERTS
General Electric Research Laboratory
Schenectady, New York

I. INTRODUCTION

A philosophical interest in vacuum can be traced back in time at least two thousand years. Aristotle explained the necessity of having a hole in the top of a barrel in order to draw wine out of the bottom by saying "nature abhors a vacuum." The experimentalists came on the scene about 1600. Galileo investigated the elevation of water with a suction pump, and his student, Torricelli, invented the mercury barometer. Since then, interest in vacuum physics and technology has increased at an almost exponential rate.

Vacuum is a general term referring to a region filled with gas at a pressure below atmospheric pressure. Therefore, when describing such a region it is necessary to characterize the degree of vacuum. Atmospheric pressure is defined to be the pressure exerted by a column of mercury 760 mm in height at 0°C. under standard acceleration of gravity of 980.665 cm sec^{-2}. Vacuum is then expressed in terms of pressure. The units used are usually mm of Hg or torr. The latter is currently preferred. One mm of Hg equals one torr to one part in 10^7.

The general classifications of vacuum are rough, medium, high, and ultrahigh. The pressure ranges corresponding to each of these are given in Table I, which also lists for each pressure, gas density, mean free path,

TABLE I

Classifications of Vacuum. The Variation of Gas Density, Mean Free Path, and Collision Frequency with Pressure

Vacuum		←Rough→	←Medium→	←High→	←Ultrahigh→
Pressure (torr)	760 (1 atm.)	1	10^{-3}	10^{-8}	10^{-13}
Density (mol/cc)	2.5×10^{19}	3.2×10^{16}	3.2×10^{13}	3.2×10^{8}	3.2×10^{3}
Mean Free Path* (cm)	6.6×10^{-6}	5×10^{-3}	5	5×10^{5}	5×10^{10}
Collisions with Surface* (mol/sec/cm²)	2.9×10^{23}	3.8×10^{20}	3.8×10^{17}	3.8×10^{12}	3.8×10^{7}

*For air at 25°C.

and molecule-surface collision frequency. As the vacuum gets higher and the pressure lower, the density decreases, the mean free path increases, and the gas-surface collision frequency decreases. It is the implications of these trends which make ultrahigh vacuum (any pressure less than 10^{-8} torr) a powerful tool for research and technology.

By using ultrahigh vacuum techniques, it has been possible to produce gases of very high purity which are required for controlled thermonuclear devices. Thin metal film cryotron devices require preparation in a vacuum which does not contribute impurities, which could alter superconducting properties. Again, this requires a low residual density of contaminant molecules in the vacuum. Electronic devices, vacuum switches, surface physical and surface chemical studies require the generation and maintenance of atomically clean metal or semiconductor films. This, too, has been made possible by ultrahigh vacuum techniques(1). The relationship between the pressure of an adsorbable gas and the time required to contaminate a clean surface is given in Fig. 1. About one second is required at 10^{-6} torr.

Ultrahigh vacuum techniques have also been applied to the space program. This is quite reasonable since the pressure about 300 miles above the earth is 10^{-8} torr, Fig. 2. By building large chambers to simulate the vacuums of space, it is possible to test components and vehicles on earth.

It is only within the last decade that vacuums of 10^{-8} torr and lower have been produced and measured. However, now the principles and techniques are well established and pressures in the ultrahigh vacuum range

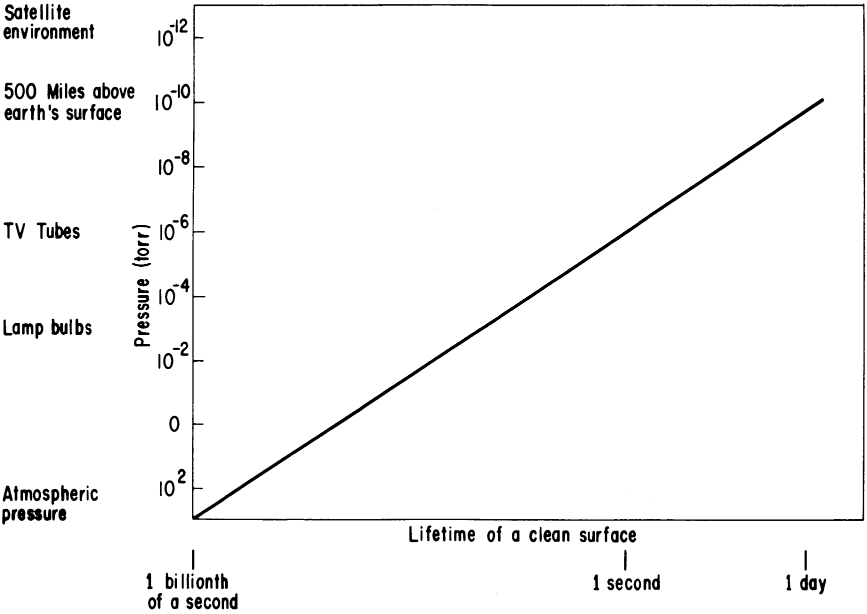


Figure I
Variation of clean surface time with pressure.

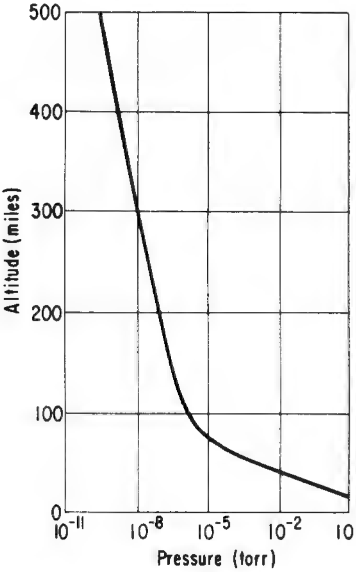


Figure 2
Variation of pressure with altitude.

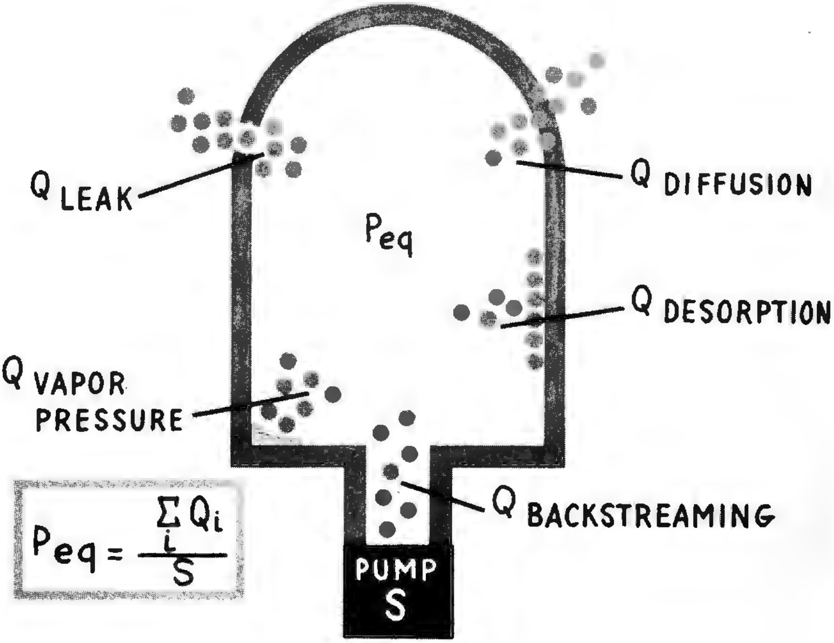


Figure 3
Schematic representation of the various sources of gas influx in a vacuum system.

can easily be produced with readily available commercial equipment. The balance of this paper will deal in a general fashion with these principles and techniques.(2)

II. ULTRAHIGH VACUUM

The equilibrium pressure, P_{eq}, in a vacuum system, Fig. 3, is determined by the rate at which gas enters the chamber and the rate at which it is removed. That is

$$P_{eq} = \frac{Q_T}{S} \text{ torr,}$$

where Q_T is the total gas influx expressed in torr liter sec^{-1}, and S is the pumping speed expressed in liter sec^{-1}. Q_T is the sum of all sources of gas entering the system and includes leaks in the system wall, permeation through the wall, desorption from the wall, back streaming from the pump, and gas evolved by high vapor pressure materials in the system. These sources are shown schematically in Fig. 3.

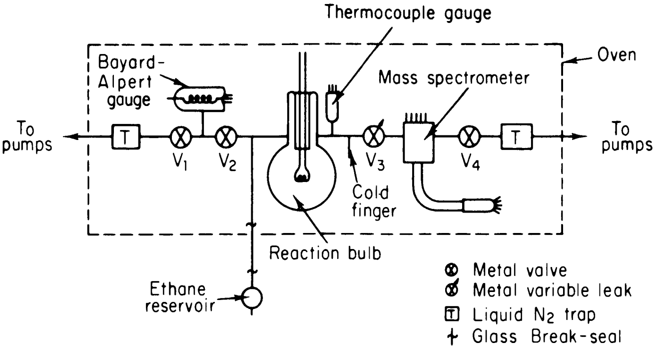


Figure 4

Schematic diagram of ultrahigh vacuum system used for studying the reaction of a gas with a clean metal film.

There are two obvious methods for reducing the pressure in the system. One is to minimize the gas influx, Q_T, and the other to maximize the pumping speed, S. The choice of either of these methods or a combination of the two is dictated by the experiment to be performed in the vacuum system. Consider two examples: a study of the reaction of a gas with a metal film, and the ground testing of a space vehicle. The vacuum system used for the gas-film study is shown in Fig. 4 and Fig. 5. It is constructed from glass and metal and can be heated to 300 or 450°C for outgassing of the parts. This results in a low total gas influx. Because of the low Q_T of this system, a five liter sec^{-1} mercury diffusion pump trapped with liquid nitrogen can pump this 2-liter volume down to 10^{-10} torr.

Testing of a space vehicle in a space simulator, Fig. 6, is quite a different story. Here Q_T is very large and bakeout is impossible. Therefore, pumps with enormous speeds must be used. Cryogenic pumps with speeds

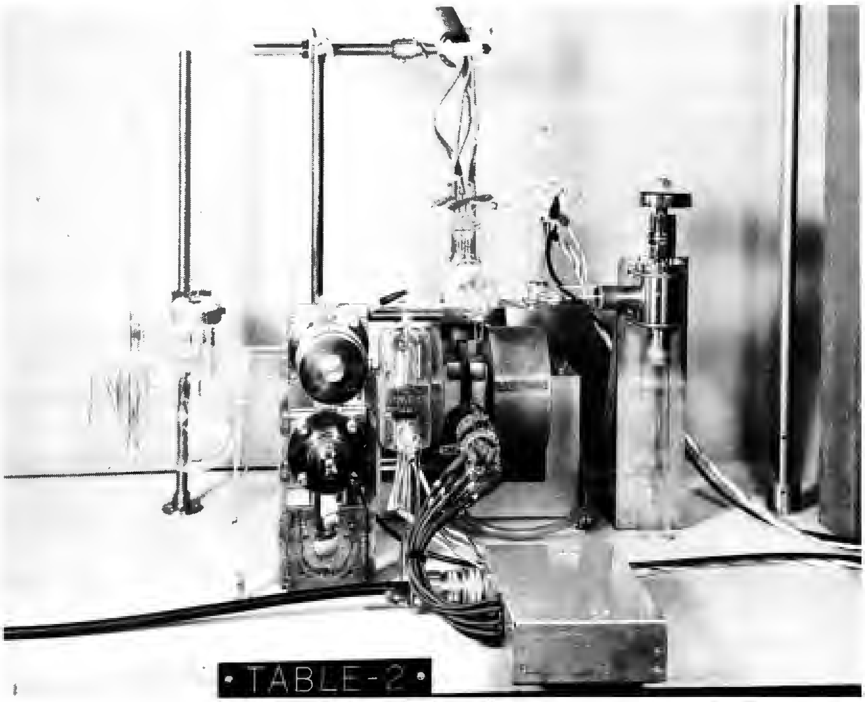


Figure 5

Photograph of ultrahigh vacuum system used for studying the reaction of a gas with a clean metal film.

of many thousands liters sec^{-1} are the primary means for removing gas in these simulators. These pumps, which will be described later, are cryogenically cooled surfaces which surround the test vehicle and remove from the gas phase a large fraction of molecules which strike the surface.

III. COMPONENTS

These two systems, while quite different, employ similar components which allow the achievement of ultrahigh vacuum. Let us disect ultrahigh vacuum systems and look at the various components and their principles of operation.

A. *Materials*

As we mentioned, one of the major considerations in the selection of materials for ultrahigh vacuum systems is to keep the gas influx to a minimum. Therefore, materials should have a low vapor pressure and should be impervious to the diffusion of gas through them at both the system operating temperature and bakeout temperature (300 to 450°C). These criteria generally preclude the use of rubber O-rings, waxes, greases, glass stopcocks and joints, brass, and soft solder found in many laboratory vacuum systems.

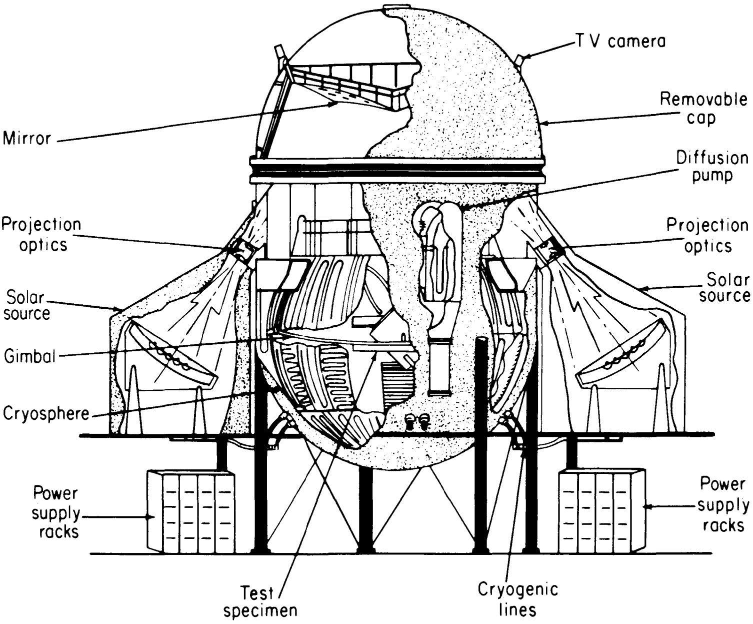


Figure 6
Schematic diagram of the General Electric M.S.D. space simulator.

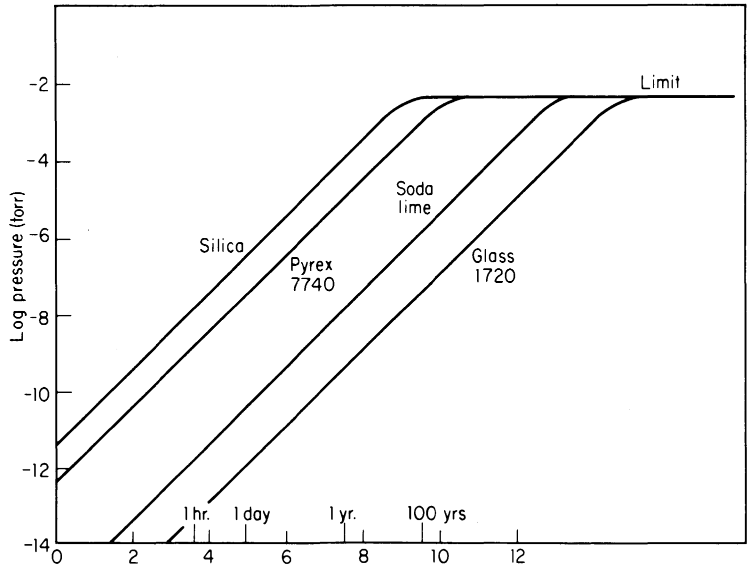


Figure 7
Helium accumulation from the atmosphere in bulbs of different glasses. Bulb has a volume of 330 cm^3, 100 cm^2 area, 1 mm wall thickness, and is at 25°C.

Probably the most common material of construction used in small laboratory ultrahigh vacuum systems is glass. However, at low pressures, the diffusion of atmospheric gases through the glass envelope may constitute a limit to the pressure which can be achieved. Norton(3) has calculated the rate of helium accumulation in glass bulbs of different compositions, Fig. 7. These data indicate that the type of glass is a very important factor in determining the degree of vacuum which can be maintained in a system, and therefore, merits careful consideration.

Austenitic stainless steels are widely used in the construction of systems. Components are usually fabricated by welding or brazing. Fernico, Kovar, copper, nickel, tungsten, molybdenum are also used. Table II lists some general features of gas permeation through materials.(3)

TABLE II

General Features of Gas Permeation

Glasses	Metals	Semiconductors	Polymers
He, H_2, D_2, Ne, Ar, O_2 measurable through SiO_2	No rare gas through any metal	He and H_2 through Ge and Si	All gases permeate all polymers
	H_2 permeates most, especially Pd	Ne, Ar not measurable	Water rate apt to be high
Vitreous silica fastest	O_2 permeates Ag		Many specificities
	H_2 through Fe by corrosion, electrolysis, etc.		
All rates vary as pressure directly	Rates vary as $\sqrt{\text{pressure}}$	H_2 rate varies as $\sqrt{\text{pressure}}$	All rates vary as pressure directly

In all, rate is an exponential function of temperature for true permeation.

A more detailed consideration of materials of construction for ultrahigh vacuum applications is given elsewhere. (2b)

B. *Pumps*

A pump is any device which removes molecules from the gas phase. This may be accomplished by transfer of momentum, condensation or adsorption, chemical reaction, or by ionization and acceleration into a surface. Many pumps involve combinations of these methods. These basic pump mechanisms are illustrated schematically in Fig. 8.

In diffusion pumps, Fig. 8a, momentum is transferred to the gas being pumped by a directed high speed vapor of mercury or oil. The working

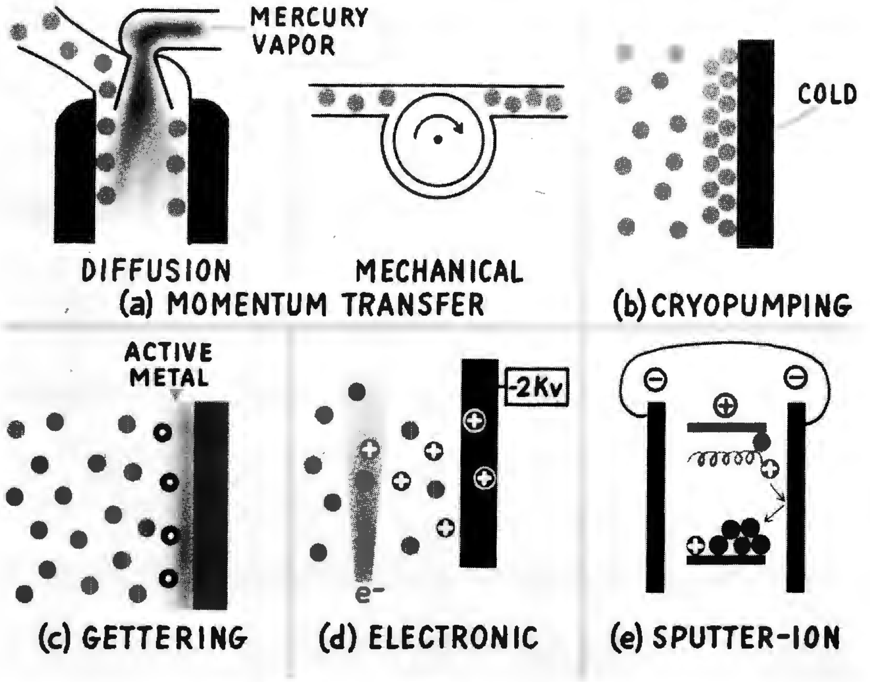


Figure 8

Basic types of vacuum pumps:

a. Momentum transfer, diffusion, mechanical

b. Condensation

c. Chemical reaction

d. Ionization and acceleration into a surface

e. Sputter-ion

fluid can diffuse into the system being evacuated unless suitable traps are provided. Zeolites are an effective trap material for oil vapor, and liquid nitrogen traps remove mercury vapor. With proper trapping, a vacuum of 10^{-10} or 10^{-11} can easily be achieved.

Momentum can also be transferred to gas molecules by a rapidly rotating surface, Fig. 8a. In these "molecular" pumps there are no mechanical seals between the input on exhaust ports and traps are not required. It has been claimed that pumps based on this principle can produce pressures as low as 10^{-9} torr.

In principle, the simplest method for removing gas from a volume is to adsorb or condense it on the walls of the vessel by reducing the temperature. If the gas is removed by condensation on a very cold surface (such that its vapor pressure is negligible), Fig. 8b, the term cryogenic pumping or cryo pumping is applied. If, however, the gas is physically adsorbed on a material of high surface area at a low temperature, the term sorption pumping is usually applied.

Sorption pumps consisting of a tube of activated charcoal at liquid nitrogen temperature have been used for years. Today zeolites are used as well as charcoal. Such pumps are often used in place of mechanical pumps in the initial pump-down of ultrahigh vacuum systems.

At 20°K (the boiling point of hydrogen at 760 torr) all gases except helium, hydrogen, and neon have a negligible vapor pressure, Fig. 9. At 4.2°K (the boiling point of liquid helium at 760 torr) all gases but helium have a very low vapor pressure. Therefore, cold surfaces at these low temperatures will act as pumps for most of the common gases.

The rate of removal of a gas depends on the condensation coefficient for the gas at the temperature of the surface and the cold surface area available. The condensation coefficient is the fraction of molecules that stick to the surface divided by the number that strike the surface. A simple calculation indicates that a liquid nitrogen cooled surface has a pumping speed of about 15 liters sec^{-1} cm^{-2} for water vapor. Because it is possible to achieve such enormous pumping speeds, cryogenic pumps are being used in large space simulators.

It is often convenient to remove chemically-active gases from a vacuum system by reacting them with an active metal to form a compound with a very low vapor pressure, or a strongly held chemisorbed layer of gas, Fig. 8c. Pumps of this type have been used for many years in the production of vacua in radio tubes and other electronic devices and are usually referred to as getters. Similarly the process of chemisorption or reaction of the metal with the gas is called gettering.

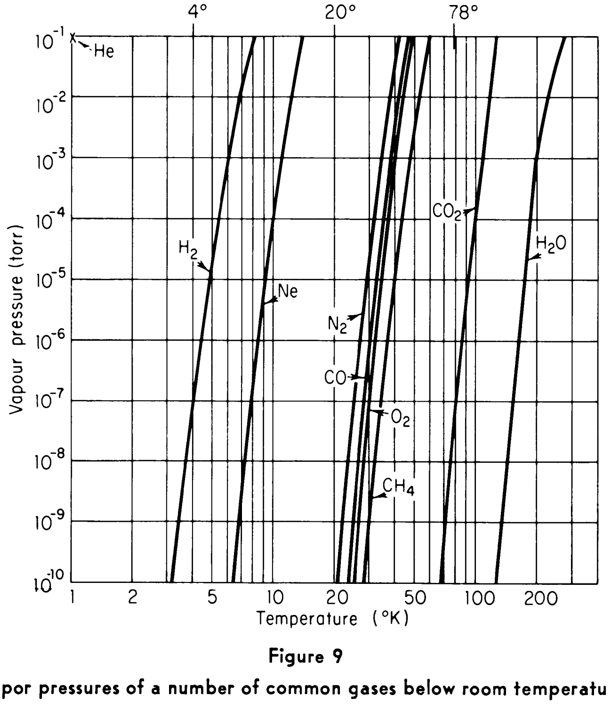


Figure 9

Vapor pressures of a number of common gases below room temperature.

In these pumps, active metal films are usually generated by the evaporation of a wire or pellet by resistance heating, or by radio frequency induction heating. Of course, the bulk getter must be carefully outgassed before evaporation or it will contribute gas to the vacuum system.

TABLE III

Classification of Metals and Semi-Metals Based on Adsorption Properties

(A indicates Adsorption, NA No Adsorption)

Metals	Gases						
	O_2	C_2H_2	C_2H_4	CO	H_2	CO_2	N_2
Ca, Sr, Ba, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Fe, (Re)	A	A	A	A	A	A	A
Ni, (Co)	A	A	A	A	A	A	NA
Rh, Pd, Pt, (Ir)	A	A	A	A	A	NA	NA
Al, Mn, Cu, Au†	A	A	A	A	NA	NA	NA
K	A	A	NA	NA	NA	NA	NA
Mg, Ag, Zn, Cd, In, Si, Ge, Sn, Pb, As, Sb, Bi	A	NA	NA	NA	NA	NA	NA
Se, Te	NA	NA	NA	NA	NA	NA	NA

† Au does not adsorb O_2

( ) Metal probably belongs to this group, but the behavior of films is not known for all gases.

Often, a metal will adsorb only a limited variety of gases. Thus, by judicious choice of a getter material, trace impurities may be removed from a gas. Table III lists a number of metals and semimetals and the gases that they will chemisorb at room temperature.(4)

Clean metals can also alter the composition of gas in a system. For example, ethane, propane, and butane will decompose on clean films of rhodium and iridium to methane.(5) It has been reported that when impure titanium getters were heated and evaporated in vacuum, methane was formed from hydrogen and carbon impurities.(6)

Titanium, molybdenum, and barium have been used extensively as getter materials. The speed of getter pumps depends primarily on the effective surface area of the getter and the sticking coefficient of the gas.

Electronic pumps, Fig. 8d, remove gas from a system by ionizing gas molecules by electron impact and by accelerating the positive ions through several thousand volts potential difference into a metal or glass surface. The adsorption and re-emission of ions from metal and glass surfaces has been investigated by many workers.(2b)

Electronic-chemisorption pumps are very effective devices for evacuating a system. They can pump chemically active and inactive gases, do not act as a source of contaminating gases, and do not require liquid nitrogen traps. These pumps contain a means for producing clean metal surfaces, a source of electrons, and an accelerating field. The potential of the metal surface is negative. Titanium and molybdenum are normally used for the getter material. Several means have been used for producing clean metal films. These include evaporation from a wire source, evaporation by electron bombardment, or sputtering.

Perhaps the most popular type of electronic-chemisorption pump is the sputter-ion pump, Fig. 8e. This pump is based on the cold-cathode or Penning discharge gauge. In its typical form, it consists of two parallel-plate titanium cathodes separated by an "egg-crate" shaped anode and located in a magnetic field. Several thousand volts are applied between the anode and the cathodes. Because of the magnetic field, electrons produced travel long spiral paths and have an increased chance of ionizing the residual gas. Positive ions produced are accelerated into the cathodes and sputter titanium onto the anode. The pumping action is a combination of gettering, acceleration of ions into surfaces, and burial of atoms. Various refinements of this pump have been developed. These include the slotted cathode pump and the third-electrode pump. These pumps are available commercially and have speeds which range from 1 liter sec^{-1} to several thousand liters sec^{-1}.

C. *Gauges*

In most systems the degree of vacuum is expressed in terms of the total gas pressure in the system. What we are really interested in, for the most part, is the particle density in the system. By knowing the temperature and the pressure, the density may be easily calculated. The composition of the gas in the system is normally expressed in terms of the partial pressure of each component. There are a variety of gauges that will measure the total pressure, the partial pressure, or the density of gas in a vacuum system.

The McLeod gauge is the standard device used to calibrate most vacuum gauges. In this gauge, the gas at an unknown pressure is trapped in a standard volume and is compressed to a known final pressure by a mercury piston into a capillary tube of known dimensions. The final volume is measured and the initial pressure is calculated from Boyle's Law. McLeod gauges may be used to measure pressures down to about 10^{-6} torr. This pressure, however, is far from the ultrahigh vacuum region.

Since it is difficult to measure low pressures directly, an indirect approach is taken. The residual gas is bombarded with electrons. Positive ions produced are collected and the current, i_+, measured. The positive ion current can often be related to the gas density, ρ, by the following expression

$$i_+ = i_- \ell Q(E) \rho$$

where i_- is the electron current, ℓ the distance the electron travels through the gas, and Q(E) the probability that a gas molecule will be ionized by an electron of energy E.

The triode ionization gauge is the device used most frequently to measure total pressures in high vacuum systems. It is shown schematically in Fig. 10a. This gauge contains a hot tungsten filament (0v potential) as a source of electrons, a grid at ~150v, and a collector at ~–20v. We find that the pressure in a system can be expressed as

$$P = \frac{1}{S} \frac{i_+}{i_-} ,$$

where S is the sensitivity of the gauge for the particular gas, i_+ is the positive ion current, and i_- is the electron current.

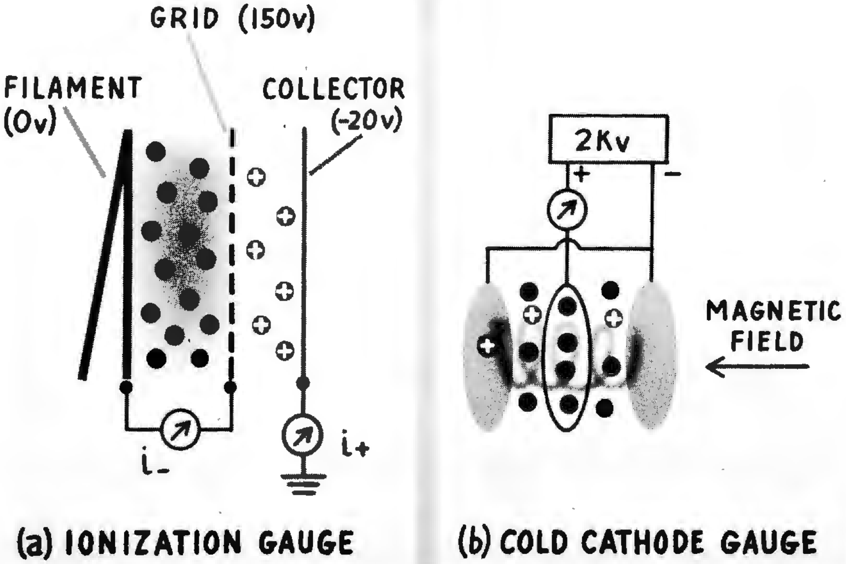


Figure 10

Vacuum gauges:

a. Triode ionization gauge b. Cold cathode gauge

One of the early forms of the triode ionization gauge took the form of a central filament surrounded by a cylinderical grid and a cylindrical sheet plate. The lower pressure limit of this structure, about 10^{-8} torr, was determined by the x-ray effect. That is, electrons that strike the grid cause the emission of soft x-rays. These x-rays strike the collector plate and produce electrons. The departure of an electron from the plate is electrically the same as the arrival of a positive ion at the collector. This limiting x-ray effect depends to a large extent on the physical shape of the collector. When the collector is massive and surrounds the grid, it intercepts practically all the soft x-rays generated at the grid.

Bayard and Alpert changed the geometry of the ionization gauge to reduce this effect. They inverted the standard gauge structure. The collector takes the form of a 0.005-inch-diameter wire surrounded by a cylindrical grid. Tungsten filaments are located outside the grid. The plate intercepts only a small fraction of the soft x-rays and the lower pressure limit is reduced to about 10^{-10} to 10^{-11} torr. This structure is called the Bayard-Alpert gauge or the inverted ionization gauge.

A typical nitrogen calibration curve for a Bayard-Alpert gauge made by the calibrated conductance method is given in Fig. 11.(7)

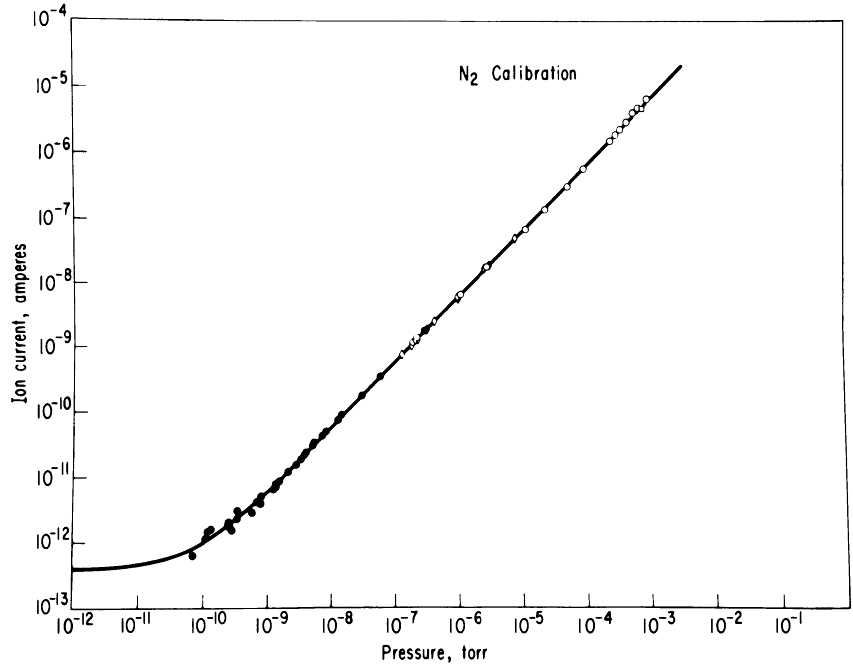


Figure 11

N_2 calibration curve for a Bayard-Alpert ionization gauge. Electron emission current is 0.5 ma.

The sensitivity of ionization gauges can be increased by increasing the effective path length of the ionizing electrons. This is often done with magnetic fields. The Lafferty(8) gauge and the Houston(9) gauge employ this method.

A class of vacuum gauges eliminates the hot filament as an electron source and uses cold emission. The Penning gauge, Fig. 10b, consists of two flat parallel cathodes separated by a cylindrical or ring-shaped anode located in an axial magnetic field. A potential of several thousand volts is applied between the electrodes. Because of the magnetic and electric field, electrons produced by cold emission oscillate in spiral paths between the cathodes. Positive ion current to the cathode is measured and is proportional to the pressure. Gauges of this type measure pressures from the ultrahigh vacuum range ($\sim 10^{-10}$ torr) to about 10^{-4} torr.(10) These gauges have a fairly high pumping speed. This property was put to use in the sputter-ion pump described earlier.

Partial pressure gauges are usually called mass spectrometers. They convert a portion of the gas into ions and measure the relative number of ions of each mass (or mass/charge, m/e) present. Mass spectrometers usually contain (1) an inlet system for the gas to be measured, (2) an ionization region in which the gas is converted to ions, (3) an analyzing region that separates the ions according to m/e, and (4) a detector that measures the number of ions for each m/e.

Ionization is usually accomplished by bombardment with electrons from a hot filament, although, cold cathode, spark sources, field ionization, and other sources have been used. Detectors are either Faraday cage collectors or ion multipliers. The latter detector is generally used at very low pressures, *i.e.*, low ion concentrations. The types of m/e analyzers vary greatly. We shall discuss only the magnetic deflection mass spectrometer.

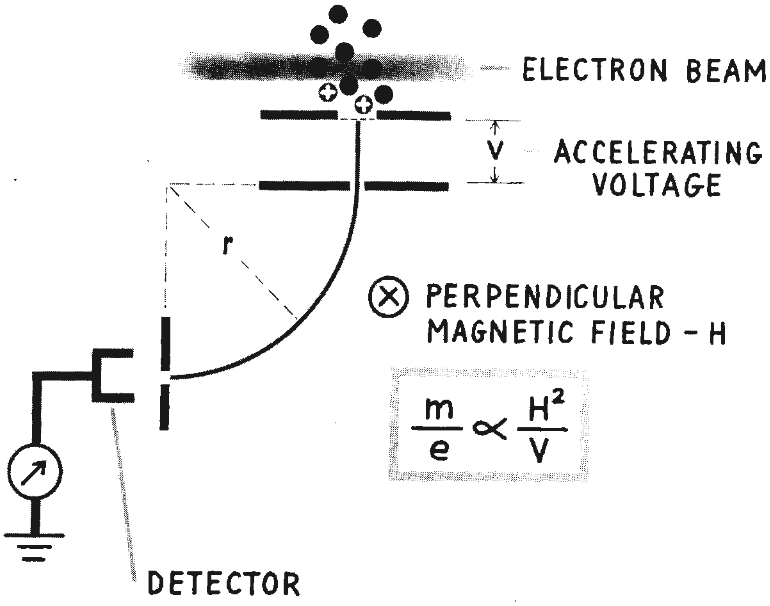


Figure 12

Schematic diagram of a magnetic mass spectrometer.

The magnetic deflection mass spectrometer is perhaps the most widely used device for partial pressure measurement in vacuum systems. A schematic diagram of a typical spectrometer is given in Fig. 12. Ions produced by electron bombardment are accelerated through a potential difference and analyzed with a magnetic field. When the ions enter the magnetic field, they experience an acceleration and have circular trajectories with a radius *r*. This radius of curvature is a function of the mass of the ion, *m;* its charge, *e;* its energy, *Ve;* and the magnetic field strength, *H.* Here V is the potential difference, and *e* is equal to *ne′*, where *e′* is the charge of an electron and *n* the number of such charges. We find that the radius is given by

$$r = \sqrt{\frac{2Vm/ne'}{H}} \text{ , or}$$

$$r = \frac{144}{H}\sqrt{Vm/n}\ ,$$

where *M* is the molecular weight of the ion.

A photograph of a typical ultrahigh vacuum mass spectrometer is shown in Fig. 13.(11)

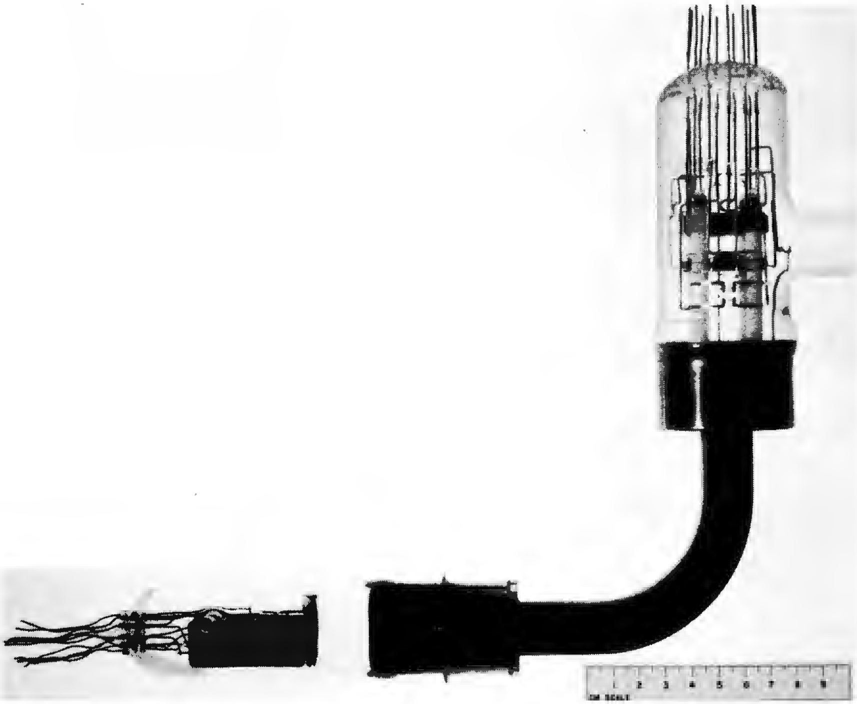


Figure 13

Photograph of a small ultrahigh vacuum mass spectrometer.

With sensitive ionmultiplier detectors and counting devices, these mass spectrometers will measure partial pressures as low as 10^{-16} torr. (12)

D. *Vacuum Seals*

Vacuum seals are generally classified as static or motion seals, and may be permanent or demountable. Today, with the increasing use of high-temperature bake-out procedures, seals are often also classified as bakeable or nonbakeable. In general, a nonbakeable seal cannot be used in ultrahigh vacuum systems. The type of seal used in a system must of course be tailored to the particular problem to be solved. Thus, while grease and rubber gaskets are widely applied in 10^{-6} torr systems, they are to be avoided in ultrahigh vacuum systems.

Permanent static seals are made by the direct joining of glass-to-glass, glass-to-metal, metal-to-metal, etc. by fusion, welding etc.

A perfect demountable seal is one in which continuous molecular contact between the two mating surfaces takes place. In practice such seals are approached with liquid metal and shear gasket seals. A number of demountable metal flange seals are shown in Fig. 14.

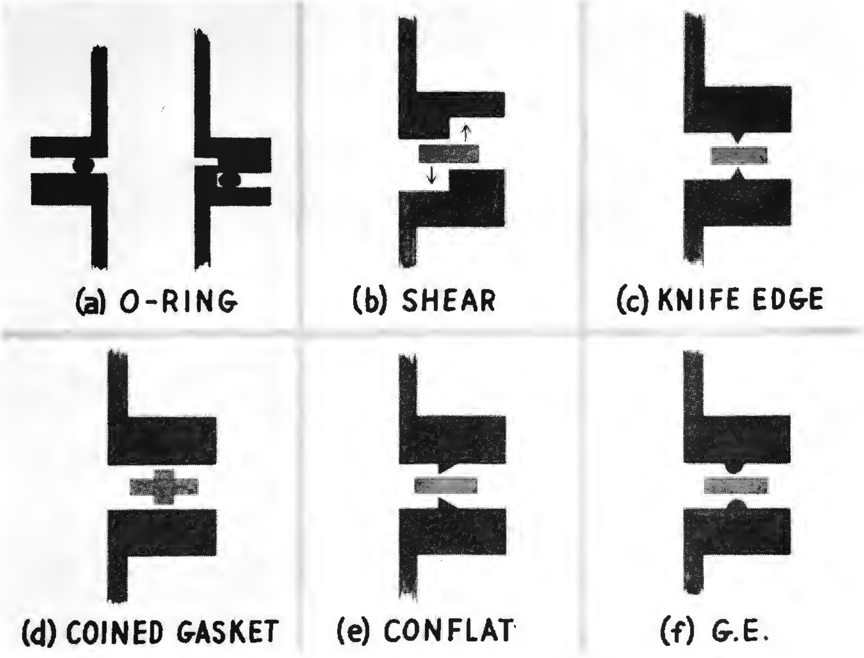


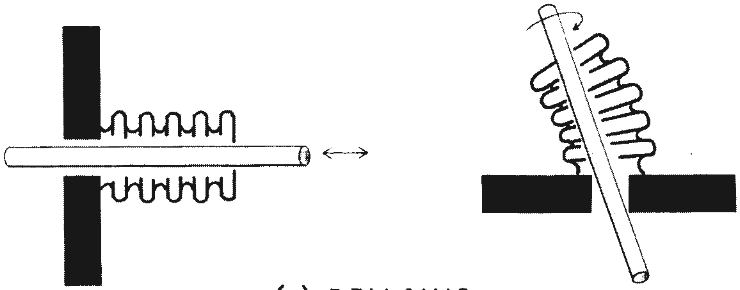
Figure 14

Ultrahigh vacuum static seals:

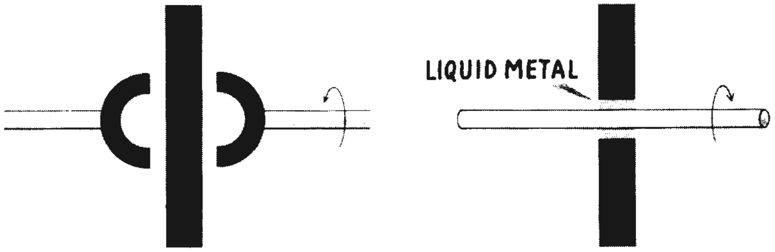
a. O-ring
b. Knife edge seal
c. Step seal
d. Coined gasket seal
e. "Con Flat" seal
f. GE seal

Metals have also been used as gasketing materials and sealing agents. Solders and low vapor pressure elements like indium have been used to seal joints. Separation is accomplished by merely reheating the joint.

Annealed gold O-rings, Fig. 14a, compressed between polished metal flanges or in a corner comprise an excellent ultrahigh vacuum seal. Aluminum, copper, and other materials have also been used. A partially sheared or compressed flat OFHC copper gasket also provides a good ultrahigh vacuum seal. A variety of flange designs have evolved. These include the knife edge seal, Fig. 14b; the step seal, Fig. 14c; the coined gasket seal, Fig. 14 d; "Con Flat" seal, Fig. 14e; and the GE seal, Fig. 14f. All of these seals will withstand high-temperature bakeout.



(a) BELLOWS



(b) MAGNETIC COUPLING

(c) DIRECT

Figure 15

Ultrahigh vacuum motion seals:

a. Bellows seals
b. Magnetic coupling
c. Low vapor pressure material seal

Several typical seals used for introducing rotary or translational motion into a vacuum are shown in Fig. 15. Metal bellows, Fig. 15a, have been used to introduce translational as well as low speed rotational motion into vacuum systems. Levers and gears may be used to amplify the motion. By using low vapor pressure materials, these seals can be used in bakeable ultrahigh vacuum systems. The transmission of motion by using the coupling of magnetic fields is another widely used technique, Fig. 15b. The vacuum wall must be made of a nonmagnetic material. Permanent magnets, or electromagnetic induction drives may be used.

Motion may also be introduced in ultrahigh vacuum systems by using a low vapor pressure liquid to form a seal around a shaft going through the vacuum wall, Fig. 15c. An eutectic mixture of gallium, indium, and tin has also been used with good results.(13) This material melts at 10.7°C and has a vapor pressure of less than 10^{-8} torr at 500°C.

E. *Valves*

Valves are an integral part of ultrahigh vacuum systems because they are used to vary conductances in the system and to isolate various parts of it.

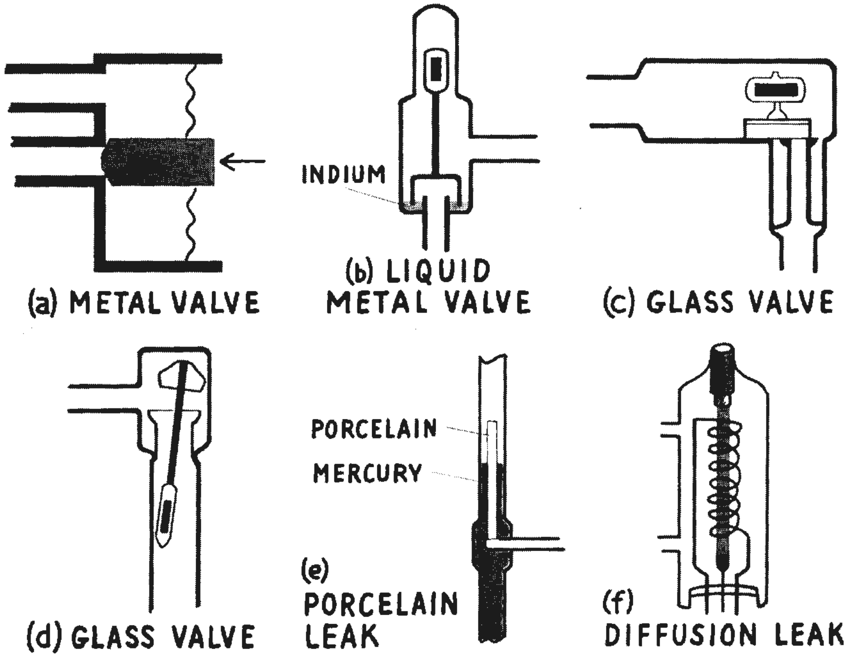


Figure 16

Ultrahigh vacuum valves:

a. Metal valve
b. Indium seal
c. Glass valve
d. Glass valve
e. Porous rod
f. Diffusion leak

Valves with the smallest closed conductance are made from metal. The sealing is accomplished by compression of a metal, shearing of a metal, or by actual melting of a metal. Motion is achieved with a flexible bellows or diaphragm, which is welded or brazed to the valve body or by magnetic coupling. A typical design for a small metal valve which employs a compression seal is shown in Fig. 16a. Many of the larger metal valves (6-inch diameter up to 14-inch diameter) actually shear the valve seat material (usually copper). In this manner a fresh seat is generated at each closure.

Indium and other low melting, low vapor pressure metals have been used as valve seat materials. They have also been used as a working fluid in cut-offs. A valve using an indium seal is shown in Fig. 16b.

Glass valves generally take the form of carefully lapped planar, Fig. 16c, or spherical, Fig. 16d, surfaces. Magnetic coupling to an iron slug incorporated in the valve is the usual method of operation. A thin glass membrane or tube and a metal-enclosed-in-glass hammer are commonly used separators. Once opened, this "valve" remains open.

A third class of valves depends on the rate of diffusion of a gas through a material. These are called diffusion leaks. Porous ceramic rods have been used as leaks. As is shown in Fig. 16e, the rod is partially surrounded with mercury and the leak rate controlled by varying the height of the mercury.

It is well known that some gases will diffuse through metals and glasses, and that the rate of diffusion is a sensitive function of temperature. A number of valves or leaks operate on this principle. They take the form of a thimble or closed tube connected to the vacuum system. The tube is surrounded by a heater wire so that its temperature can be controlled, Fig. 16f. Palladium and nickel tubes have been used for hydrogen and deuterium leaks, silver for oxygen and 96% silica glass for helium.

IV. SUMMARY

The experiment to be performed in the vacuum system dictates to a large extent the overall system design. Specific pumps, gauges, and accessories can then be selected to meet the requirements. A general rule of thumb for producing the lowest pressure is to keep sources of gas influx low and pumping speeds high.

ACKNOWLEDGMENTS

The author would like to thank W. A. Gilhooley, Jr. and M. J. Willey, Jr. for several interesting discussions.

REFERENCES

1. R. W. Roberts, "Generation of Clean Surfaces in Vacuum," *Brit. J. Appl. Phys.* **14**, 537 (1963).
2. A portion of this material is based on
   a. R. W. Roberts, "A Course in High Vacuum Technology," General Electric Research Laboratory Report No. 63-RL-3394C, August, 1963, and
   b. R. W. Roberts and T. A. Vanderslice, *Ultrahigh Vacuum and Its Applications,* Prentice-Hall, Inc., Englewood Cliffs, N. J. (1963).
3. F. J. Norton, "Gas Permeation Through the Vacuum Envelope," *Transactions of the Eighth National Vacuum Symposium*—1961, Pergamon Press, New York (1962), pg. 8.
4. G. C. Bond, *Catalysis by Metals,* Academic Press, New York (1962) pg. 66.
5. R. W. Roberts, "Adsorption and Decomposition of Hydrocarbons on Clean Metal Films," *Brit. J. Appl. Phys.* **14**, 485 (1963).
6. L. Holland, L. Laurenson, and P. G. W. Allen, "Evolution of Hydrocarbons from Impure Titanium Getters," *Nature* **192**, 749 (1961).
7. W. D. Davis, "Gauge Calibration in the Ultrahigh Vacuum Range," *Transactions of the Tenth National Vacuum Symposium*—1963, The Macmillan Co., New York (1963), pg. 253.
8. J. M. Lafferty, "Hot Cathode Magnetron Ionization Gauge for the Measurement of Ultrahigh Vacuum," *J. Appl. Phys.* **32**, 424 (1961).
9. J. M. Houston, "Ultrahigh Vacuum Ionization Gauge," *Bull. Am. Phys. Soc. II*, **1**, 301 (1956).
10. J. R. Young and F. P. Hession, "A Cold Cathode Discharge Gauge for Ultrahigh Vacuum Use," *Transactions of the Tenth National Vacuum Symposium*—1963, The Macmillan Co., New York (1963), pg. 234.
11. W. D. Davis and T. A. Vanderslice, "A Sensitive High Speed Mass Spectrometer for Ultrahigh Vacuum Work," *Transactions of the Seventh National Vacuum Symposium*—1960, Pergamon Press, New York (1961) pg. 417.
12. W. D. Davis, "Getter-Ion Pumping and Partial Pressure Measurements Below 10^{-11} Torr," *Transactions of the Ninth National Vacuum Symposium*—1962, The Macmillan Co., New York (1962) pg. 363.
13. N. Milleron, "Utilization of Surface Tension of Liquid Metals in Making High Vacuum Seals," *Transactions of the Fourth National Vacuum Symposium*—1957, Pergamon Press, New York (1958) pg. 38.

SOME RECENT CONTRIBUTIONS TO FUSED QUARTZ TECHNOLOGY

VINCENT C. DEMARIA
Thermal American Fused Quartz Co.
Montville, N. J.

New fused quartz products frequently require new fabricating techniques, before these items can be successfully marketed. Since the volume of fused quartz laboratory ware is far below that of borosilicate glasses, manufacturing new items does not require full automation methods. The real problem is in keeping pace with the growing demands for small quantities of diversified items, often commonly available in borosilicate glasses. In some cases, methods used for forming lower softening glasses apply to fused quartz, but in many instances new approaches are required to solve the problem.

Another area which invites new techniques is in the improvement of quality or manufacturing cost of established lines. An example is adhesion or molecular sealing of optically polished plates such as are used in spectrophotometer cells and Brewster angle windows on gas laser tubes. In this form of sealing, both surfaces to be joined are polished to near perfect optical flats. The parts are then wrung together and further held by external pressure or internal vacuum. Subsequent heating at temperatures below the strain point produces a strong vacuum tight seal. The finished seal has less distortion than those produced by open flame techniques.

To further indicate the present state of the art, a number of products, resulting from recent developments, have been selected for presentation because of their interest to scientific glassblowers. One such item is heavy wall fused quartz tubing which can now be produced in sizes not commercially available and of greater importance in small quantities and with tolerances unsuitable to standard tube drawing methods.

A number of heavy wall tubes are shown in Fig. 1 that were made by a recently developed process. Sizes of 10 mm I.D. by 20 mm O.D. are typical, but bore sizes down to 2 mm and O.D.'s up to 40 mm are practical. Inside diameters of ±0.002″ are standard over 24″ lengths and when necessary outside diameters can be ground and polished to within a few ten thousands of an inch. Tubes with 6 to 8 mm wall may be fabricated into rugged apparatus, however, the intense heat required to penetrate usually limits the applications to high pressure tubes and for flat flanges that are sliced off and fused to tube ends to eliminate drilling of plate. The short tapered piece in the center was drawn down in an oxygen-propane gas crossfire flame at the lathe.

The precision bore capillary tube (Fig. 2) has an I.D. of 0.003″ and an O.D. of 8 mm. It was produced by what we believe to be the first commercially feasible method of making fused quartz thermometer tubing. To simplify the thermometer makers job, blanks are supplied with sufficient bulb length to accommodate various temperature ranges.

You may ask why fused quartz thermometers? Because of the inherently low hysteresis of the material, which stabilizes the initial pre-

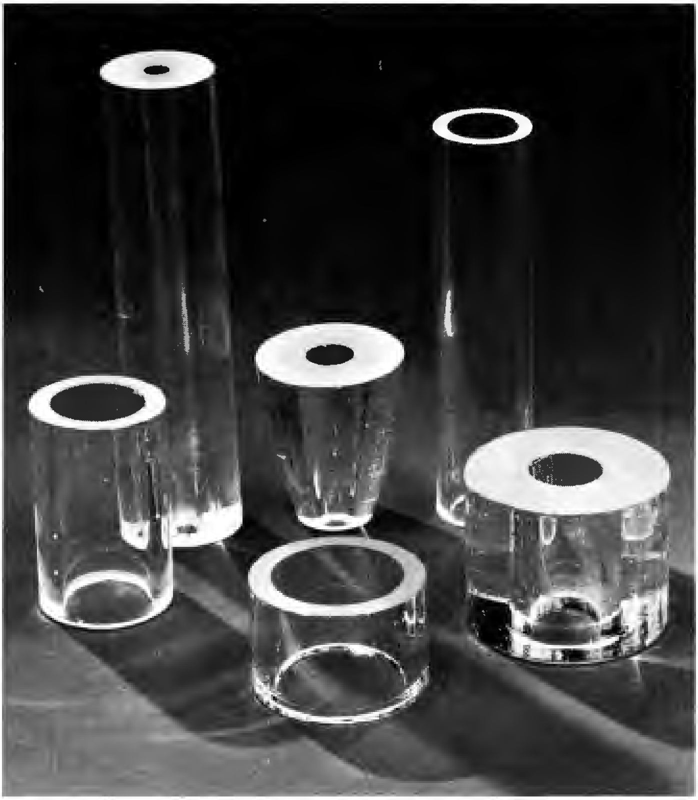


Figure I

A new forming technique makes possible a wide range of heavy wall fused quartz tubes. Small production runs and close tolerances are inherent features of the new method.

cision calibration. Moreau, Hall and Leaver[1] found that thermometers having a range of 0-28°C show a reproducibility of ±0.0007° Centigrade over a 12 month period and heated for a month at 100°C did not produce a change greater than 0.001°C. Ultra precision kinematic viscosity thermometers would have their entire scale calibrated over a 2° range of required temperature.[2] In addition, gallium filled fused quartz thermometers can withstand high thermal shock environments and temperatures in the 1000°C range. The general use of fused quartz thermometers has depended on the manufacture of the necessary tubing. Thermometers made from tubing as shown here are not as yet available, but are now being tested and may soon be the answer to an old problem.

The techniques developed for drawing thermometer tubing have also led to precision micro and macro tubing (Fig. 3). Tolerances of plus or minus two to three thousandths on inside and outside diameters are normal for applications as electronic insulators, mold cores and special analytical cells. Wall thickness as thin as .005″ can be produced and concentricity ranges between .0005″ and .001″, depending on diameter.

Odd shaped tubing (Fig. 4) is well known to users of fused quartz. Here again, as in the case with heavy wall tubing, small quantities are frequently requested in a wide variety of shapes and sizes. Special techniques in fused quartz forming and machine shop tooling had to be devised to handle the problem so that precision dimensions could be produced without high tooling costs. The figure shows how "odd-shaped" fused quartz can be made. The majority of shapes are precision vacuum formed on mandrels in 30″ lengths. The preformed tubing tolerances are

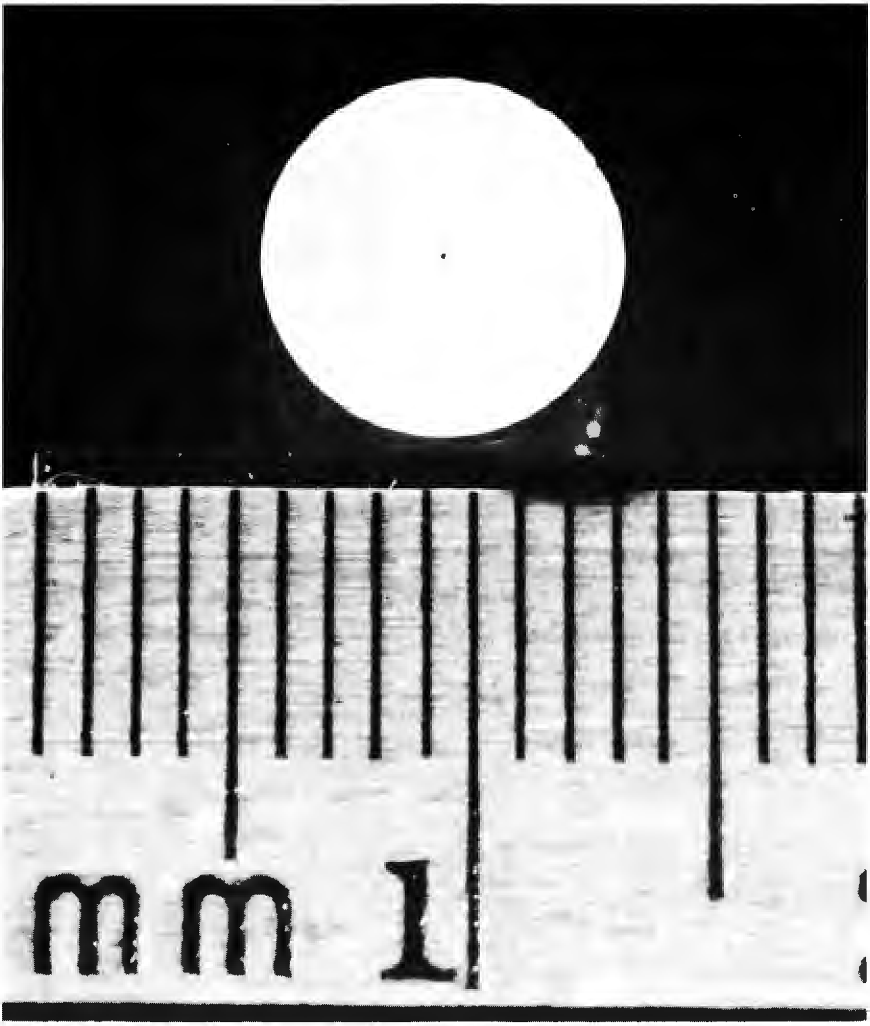


Figure 2

Fused quartz thermometer tubing, with a .003″ bore, has evolved from refinements in heavy wall tubing manufacture. Calibration and testing are presently in the development stage.

Figure 3
This assortment of micro and macro tubing is machine drawn with tolerances of ±.002 of an inch.

Figure 4
Special forming methods cater to laboratory quantities of vacuum formed tubing in a wide variety of shapes and wall thicknesses.

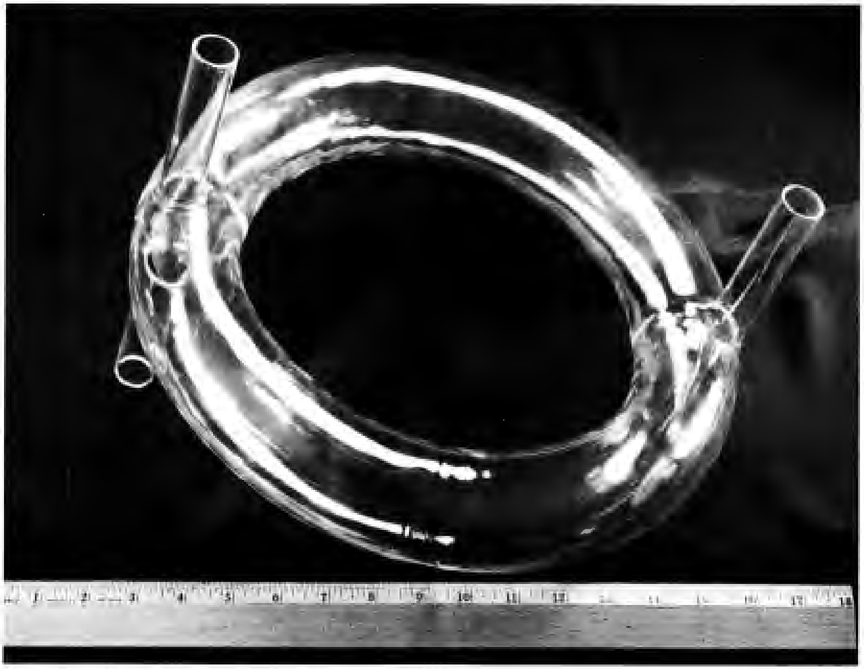


Figure 5

Machine made half circles were fused at the bench to produce this torus from 64 mm. tubing.

similar to stock round tubing for equivalent sizes. As can be seen, thin standard or heavy walls may be produced by this method.

Some of the tube shapes are sliced in half and end plates fused on to produce trays and boats. A recent application for the heavy wall rectangular tube was for encapsulating graphite slabs. This forms a high temperature, non-contaminating hot plate within a vacuum system when inductively heated. When encapsulating, two precautions should be observed; first the wall thickness must be heavy enough to prevent collapse of the wider flat surface, and second, the entire tube and sealed-in graphite slab must be heated above the ultimate operating temperature, while evacuated, before tipping off. The two irregular shaped tubes have all precision inside dimensions and are used in the steel industry.

The doughnut, or so called torus (Fig. 5), is made from 64 mm O.D. tubing and is wound on a 6″ radius. Because of the ratio of tube diameter to the circle radius, the inside wall thickness becomes almost twice that of the outer circumference wall. Machine made half circles were sealed together at the bench; at this time the side arm tubes were added. The splice at the bottom of this circle was made at the glass lathe before the tubing was bent. As can be realized, a doughnut thirty inches in diameter may be formed with less effort than this small radius tube. The glassblower's problems of winding a fused quartz coil at the bench or lathe are as numerous as making a stock item flask or ground joint. For this reason, machine made coils, in a wide variety of diameters and lengths are available for assembly into fused quartz apparatus or special lamps.

In Fig. 6 we see a new approach to coil winding. This helical coil lamp or water jacket is constructed from two cylindrical tubes, nested to provide a desired annular space. By a new sealing process the walls of both tubes are brought together, and fused along a narrow helical path. The joint is completely fused leaving no trace of an interface. The wall thickness at the seal is not doubled, as might be expected, but closer to the wall thickness of one tube. Helical bore shapes can be varied, as shown in the cross sectioned segments. At the present time, tube diameters range from one inch to four inches. Some features of this construction are ruggedness over spring-like tubing coils, especially in lengths over 12 inches. Precision tolerances are possible on the inner and outer diameters because the selected tubing sizes are not distorted, except at the helical fusion line. This construction provides a new concept for the lamp designer in that reflectors can be fired directly onto the lamp body or the continuous inner tube may be used for water cooling.

Apparatus for irradiation of blood plasma or photochemical reaction tubes appear possible. Joints, graded seals, or standard tubing may be fused to the large open ends when the helical inlet and outlet tubes are at right angles to the axis, to form a variety of special apparatus.

Figure 6

Rugged helical coils can now be produced in long lengths from two cylindrical tubes. The nested tubes are fused together along a narrow helical path by a new sealing process.

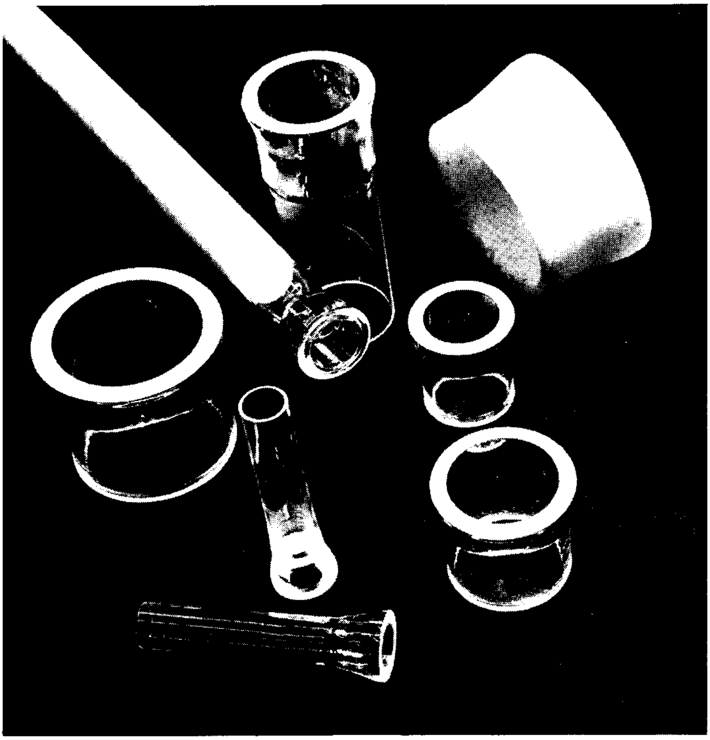


Figure 7

The production of fused quartz conical pipe flanges have recently uncovered new pressing techniques which simplify heavy wall fused quartz fabrication.

Fused quartz conical pipe flanges (Fig. 7) match the dimensions of standard borosilicate glass pipe. The smaller flanges in this photograph are of particular interest because their manufacture represents a giant step in the forming of fused quartz. They are produced by a blow and press process which maintains close tolerances at lower cost than tooling or grinding. Fused quartz pipe flanges and "O" ring flanges are finding wider application for demountable joining to borosilicate glass or metal systems because they can be used without grease.

Two new fabricating processes are shown (Fig. 8) in the form of crucibles. The crucible on the left appears to be a standard crucible but has a thin veneer of ultra high purity Spectrosil on the inside and a heavier external layer of commercial grade fused quartz. By this economical method flasks, beakers, boats, etc. can be produced with internal surfaces having total metallic impurities of less than 0.2 parts per million and a boron content of less than one hundredth of a part per million.

The crucible on the right illustrates how thin wall fused quartz, having little mass to retain heat, can be mold blown. By using this new blowing method, four inch diameter cells with .010″ wall have been formed

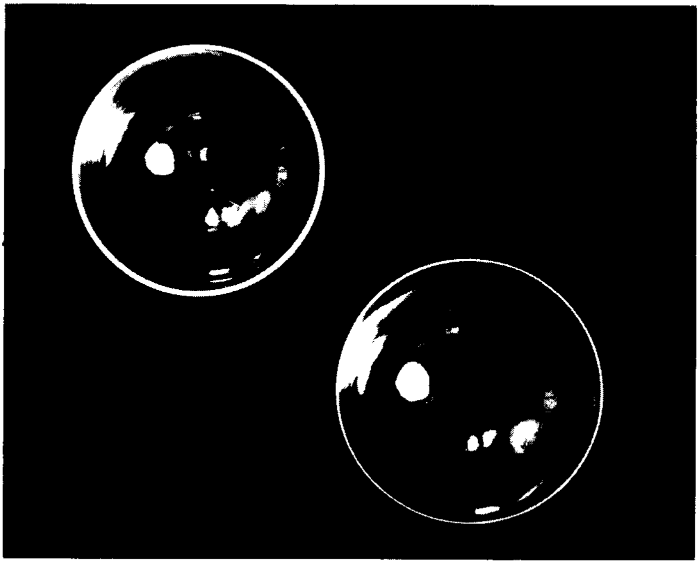


Figure 8
The crucible on the left has a thin veneer of ultra high purity Spectrosil on the inside and a heavier external layer of commercial grade fused quartz. The crucible on the right illustrates how thin wall fused quartz, having little mass to retain heat, can be mold blown by a new blowing method.

in spite of the narrow working range of fused quartz which normally causes it to become rigid on removal from the flame.

The economic advantage of thin wall ware makes possible disposable containers that have become devitrified after a single high temperature use.

Improved manufacturing techniques have resulted in eliminating many of the old difficulties experienced in supplying fused quartz. These improvements have made available a wider range of shapes and sizes of commercial ware. It is hoped that continued efforts in this direction will further simplify the scientific glassblowers task of constructing apparatus from the ideal glass—fused quartz.

REFERENCES

1. "Mercury-in-quartz Thermometers for Very High Accuracy"—H. Moreau, J. A. Hall, and Vera M. Leaver, *J. Sci. Instr.*, **34** (4) 147-54 (1957).
2. Private communication—V. Hiergersall, H. B. Thermometer Co., Phila., Pa.

QUARTZ - SILICA - LUCALOX

ROBERT J. SOMMER
General Electric Co.
Cleveland, Ohio

In the time since last year's meeting some interesting developments have taken place and I am most happy to again have the opportunity of discussing Fused Quartz and Lucalox® ceramic with you. Bill Gilhooley, will follow in a very short time with an interesting description of work he has done in making glass to ceramic seals—including Lucalox-to-glass seals. This will be an introduction to his demonstration of this technique tomorrow afternoon.

Last year I mentioned that we had under development a new fused silica with superior characteristics in terms of:

(1) U V Transmission
(2) Homogeneity—Schlieran
(3) Absence of inclusions and bubbles

This material is now being marketed and is designated as Type 151 Fused Silica. This first slide (1) will give you an appreciation of the improvement in ultra violet transmission that has been attained. You will note that whereas our other quartz materials do not have high transmission much lower than .20 microns, Type 151 exceeds 80% transmission for 1 cm thickness at .18 microns. Type 151 does show the characteristic water absorption band in the infra-red. In addition to its excellent U V transmission, Type 151 has superior quality for homogeneity—or uniformity of index of refraction. Note 105-106 curve for full range of quartz transmission. For example, this slide (2) shows a shadowgraph comparison of Type 151 and one of our lower grade materials. Note the uniformity and absence of shadows. This is important for transmission applications of the most critical kind—and Type 151 is free of bubbles and inclusions. Here in this slide (3) (Figure 1) you will see a few samples of this grade.

As a result of the extremely high purity of Type 151, it is resistant to darkening due to exposure to radiation. As this table (4) shows, the transmission has been essentially unaffected even after treatment of 10^6 roentgens of gamma radiation. Similar results are obtained in the case of high speed electron radiation.

Another manifestation of the purity of this silica is the absence of fluorescence under ultra violet excitation. While many quartz or silicas exhibit either a yellow-green or purple fluorescence this is not evident in Type 151. This is an important consideration in certain U V transmission applications.

Type 151 has proven to have substantial advantages for a variety of applications, and I'll mention just a couple:

Lasers—as mentioned because of its homogeneity—Type 151 is an excellent material for Brewsters Angle windows. Using standard JAN G 174 testing, Type 151 pieces were rated grade "A" when viewed in all

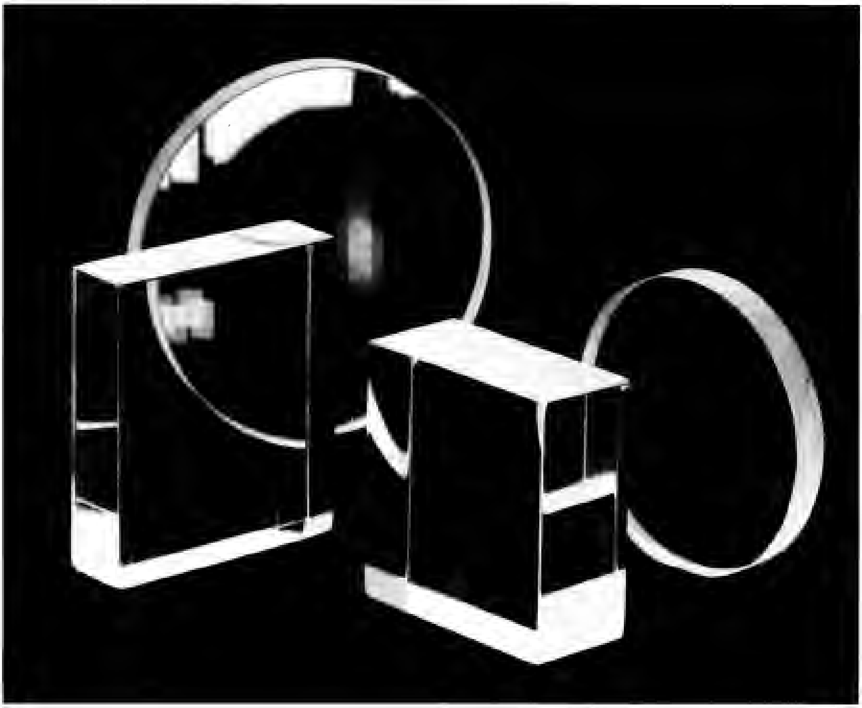


Figure I

directions through the piece. Currently, evaluation testing in Laser applications is under way.

Spectrophotometer Prisms, Cells and Lenses—because of its high transmission in the far ultra violet—a number of manufacturers have tested and found Type 151 ideally suited to this type of application.

In working Type 151, we have used the same techniques that were previously used with our solid shape materials. We have found that the working temperature is somewhat lower for 151. This might be attributed to the water content of the material. Windows have been readily fabricated into the side and ends of tubing.

So, much progress has been made in this area. Let's talk a little bit about Lucalox as a prelude to Bill Gilhooley's discussion of how to work with this interesting material. Again, over the past year a number of applications have been found and I would like to mention a few of the most intriguing. As you know, Lucalox was first developed as a lamp material. A lamp utilizing Lucalox as the container for the arc has been developed—

and this light source promises to just about double the efficiency presently realized from the conventional mercury lamp. This means twice the light for the same wattage input—a real breakthrough.

Recently RCA has utilized Lucalox in an unusual application. One problem with scintillation counters is the background radiation which emanates from the components of the instrument—and particularly the window through which the energy passes and which seals off the sensing element. Because of the extreme purity of Lucalox and the low radiation background of the material, its use has simplified nuclear detection systems. In addition RCA found that Lucalox was readily adaptable to electron tube envelope construction in the ceramic-to-metal seals are an established manufacturing procedure. The scintillation counters using Lucalox windows were introduced in February. We are of course pleased with the performance of Lucalox in this interesting application.

Another area of active interest involves the use of Lucalox for gas bearing gyros. Because of its density and the absence of pores, Lucalox can be finished to much finer surfaces than conventional aluminas. This slide (6) shows a profilometer tracing of a very finely polished Lucalox surface. You will note that occasionally a dip will occur in the surface. This is a result of grain pull-outs which are generally traceable to limitations of polishing technique. Even so, these defects are widely dispersed and the overall finish greatly exceeds that which has been previously attainable on polycrystalline alumina ceramics. This has resulted in significant improvements in highly critical guidance devices.

As glass blowers, you will be interested in methods of joining Lucalox to other materials and I'm sure you will be particularly interested in the talk on Lucalox to glass seals.

I mentioned that RCA has found that conventional electron tube sealing techniques worked well with Lucalox. We do not make Lucalox to metal seals, however, over the past year a number of companies in this business have successfully made Lucalox to metal seals and we are now in a position to supply this type of product utilizing the capabilities of these manufacturers.

This slide (7) shows some examples of hermetic seals which have been fabricated by these suppliers. Included in this overall capability are seals to moly, copper, kovar, etc. Generally the base is a moly manganese coating on the Lucalox followed by a nickel plate. At this point the nickel can be brazed to a wide variety of materials. The higher temperature materials are used for sealing Lucalox lead-in insulators into thermionic converter devices which may operate up to 1000°C and in highly corrosive cesium vapor atmospheres. In this case it is highly important that no glass phase exist either in the seal material or the ceramic—this is one of the reasons Lucalox has proven to be useful—it has no glass phase. Of course for lower temperature and less corrosive application more simplified seals can be utilized.

An example of this would be the sealing of Lucalox to stainless steel, Type 430, for a microwave window application. Dielectric loss factor is a measure of the transparency of the material to microwave energy. Lucalox will transmit about twice the amount of microwave energy when compared to other types of polycrystalline aluminas. These transmission windows are necessarily hermetically sealed to the power tube structure. Conventional techniques which have been used with aluminas seem to work as well with Lucalox.

The finishing of Lucalox after firing is much the same as quartz and glass in terms of the materials used. Lucalox of course, is much harder than the glass materials—it is 9+ on the mohs scale as compared to 4.9 for quartz. Its extreme hardness (which is characteristic of aluminas generally), coupled with the good finish, led us to believe that Lucalox might find wide use in wear applications. For instance—dies. Our experience has shown that while Lucalox might have promise for some specialty die applications, it appears it is not suitable for hi-carbon steel and copper wire drawing—evidently grain pull-out contributes to excessive wear. On the other hand, tests on varieties of Lucalox for use as cuttings tools has shown some promise and Lucalox spheres are being used in ball valves where wear cannot be tolerated. So it appears that Lucalox will have some specialized wear application.

Cutting of the fired material is done with a diamond wheel—much the same as quartz. Finished Lucalox can be diamond ground (slide 8) and this slide shows some pieces that have been threaded and some of the spheres I mentioned. Generally Lucalox is polished starting with a 240 grit diamond wheel, then 9 micron diamond paste on a brass lap followed by 6, 3, and 1 micron pastes on the same lap. In handling Lucalox, of course, as with any brittle material, scratching and chipping should be avoided since this results in the creation of stress raisers. Also, as in good design practice sharp corners should be avoided.

Again, I appreciate discussing quartz and Lucalox with you. We always look forward to this meeting and the opportunity of participating in your program. Now I'll let Bill take over. Thank you very much.

SEALING GLASS TO CERAMIC FURNACE TUBES

William A. Gilhooley
General Electric Research Laboratory
Schenectady, New York

Due to the emphasis being placed on high temperature experimentation, ceramic furnace tubes are being used more extensively for many applications in the Laboratory. Ceramic furnace tubes are impervious to air to approximately 1900°C. and to dry hydrogen and carbon monoxide to approximately 1300°C. This of course is much higher than 96% silica glass or quartz can be used under these same conditions.

For many applications it is desirable to connect these ceramic tubes to a vacuum system so that all the air can be pumped out and some other gas such as hydrogen, nitrogen, etc., can be introduced with the experiment. Therefore a vacuum tight glass to ceramic seal must be made.

There are various types of ceramic tubing available. The physical properties of the ceramic and the temperature at which the furnace is to be operated will be the governing factor in determining the type of ceramic you will choose.

After selecting the type of ceramic we must now select the glass to be used. The glass we use must have a coefficient of expansion closely matching the ceramic. Some of the various ceramics and their matching glasses are as follows:

English Mullite
McDaniel MV 30 = Corning 7720 glass
McDaniel MV 33
Porcelain = Corning 7740 glass
High Grade Alumina = Corning 7520 glass
Corning 7530 glass

Coefficient of expansion of high grade alumina sometimes varies enough so that if 7520 glass does not work we use 7530 glass.

Before starting the actual sealing, something should be said about preparing the materials for sealing. The glass should be cut square and fire polished or flame cut. The wall thickness of the glass at the point where it is to be sealed to the ceramic should be about the same thickness as the ceramic. The ceramic should be cut square on a diamond wheel. Then the outside of the sealing edge should be slightly rounded so as to eliminate any chips that may have occurred on the cut off saw. This can be accomplished by rotating the circumference of the tubes on a belt sander or the side of the cut off saw blade. Then the ceramic should be cleaned in distilled water and dried. At this point the ceramic should be inspected so as to be sure that there are no chips or cracks at the sealing edge. Inspection under a microscope is desirable.

The glass and ceramic are now placed in a glass blowing lathe with provisions being made so that you can blow into the work. The ceramic is slowly heated with a bunsen burner. The bunsen is placed so that it heats the ceramic about 5″ back from the sealing edge. Increase the heat of the bunsen burner slowly until the ceramic begins to show an orange color at the sealing edge, then turn on the lathe fires, again slowly bringing the ceramic up in temperature. Bring the glass up to about ⅛″ from the ceramic. When the glass is molten at the sealing edge butt the ceramic and glass together keeping the fires on the ceramic. Heat the ceramic to approximately 100° hotter than the working point of the glass; in this way the ceramic will radiate enough heat to make a good seal. (Care should be taken so that you do not heat the ceramic more than 100°C. hotter than the working temperature of the glass because if the ceramic is overheated it will tend to boil and crystallize.) While the seal is being made the bunsen remains under the ceramic adjacent to the sealing edge.

After the seal is made, flame anneal the glass and bring the ceramic and glass to an ambient temperature slowly. Remember the glass will cool much faster than the ceramic. Smoke the seal down, that is; build up a layer of lamp black on the glass and ceramic and allow this lamp black to remain until the seal is at room temperature. This method is used to seal glass to English mullite, McDaniel MV 30 & MV 33 and porcelain.

In the second category we have a group of ceramic materials which, because they will not stand up under localized heating, must be handled differently. In this group we have the following ceramics with their matching glasses listed:

G. E. Lucalox — 0080 glass
Recrystallized alumina — 7280 glass
Normalized Zirconia — 0080 glass

To make these ceramic seals we prepare the ceramic and glass the same as we would for any type of ceramic seal.

After we have the ceramic and glass set up in the glass blowing lathe ready for sealing, we now take a piece of 96% silica glass tubing about 1″ to 1½″ larger in diameter than the ceramic and glass. This tube is set up in a ring stand and placed so that it acts as a furnace around the glass and ceramic. The glass to be sealed is moved out of this tube so that it does not get hot and deform before we are ready to make the seal. Now we heat the 96% silica glass at the point where the ceramic and glass seal is to be made with either a torch or lathe fires. Be careful in heating because while the ceramic and glass are turning, the outer 96% silica glass is not turning and by spot heating such as we are doing, we can burn a hole in it. If this happens and the flame touches the ceramic it will crack the ceramic. We heat the outer tube hot enough so that it radiates enough heat to bring the ceramic above the working temperature of the glass being sealed. When the ceramic is sufficiently hot enough to make the seal we move the glass up next to the ceramic. When the glass gets almost molten (before it deforms) we butt the ceramic and glass together. Keep the heat on long enough to work the glass sufficiently to make a good seal. The heat of the torch or lathe fires can now be reduced. Allow the lathe to rotate and continue to heat the 96% silica glass tube which will anneal the ceramic to glass seal. Then reduce the heat and bring the seal to room temperature.

These seals have all been made repeatedly at the G. E. Research Laboratory with a great amount of success.

LOW TEMPERATURE GLASS SEALS

MORRIS LIEBSON
IBM Watson Research Center
Yorktown Heights, New York

The title of this paper is a misnomer, for there are very few methods whereby glass can be hermetically sealed to itself without raising its temperature to a considerable degree. However, various expedients can be devised to seal delicate apparatus into glass envelopes with little, or no, rise in temperature of the apparatus so sealed. Some of the methods for accomplishing this, and used with varying degrees of success are:

1. Flanged joints
2. Ground joints
3. Use of waxes, greases, or cements
4. Poly optic technique
   - (*a*) indirect heating
   - (*b*) direct heating
   - (*c*) arc-sealing
6. Solder glass techniques
7. Use of epoxy cements
8. Thermo-compression bonding.

Flanged joints, ground joints, and the use of waxes and the like, or any combination of these with one possible exception, have one serious drawback. They cannot be baked at high temperatures. The exception occurs when a metal gasket is used in combination with the flanged joint, a rather expensive method of sealing glass.

The idea of baking out devices sealed in glass may seem to be at variance with the purpose of this paper. This is not so, for the bake out temperature of a glass such as the borosilicates commonly used for laboratory purposes, is usually 450°C., whereas its working point is usually well above 1,200°C. In addition, bake out is almost invariably done with the internal structure in vacuum where oxidation cannot take place; in fact, many materials are subjected to vacuum bake out in order to reduce oxides and effect "clean up". In addition, the use of waxes, greases, or cements is usually poor practice in high vacuum work, for these materials all have comparatively high vapor pressures, and therefore, may degrade any vacuum in which they are present. These three glass joining methods, however, do have the advantages of being readily demountable, require very little skill for assembly and disassembly, and can provide a seal sufficiently tight for most laboratory purposes. It is interesting to note that the use of flanged joints in glass assembly is becoming increasingly popular, at present, and that all the major fabricators are marketing flanged joints, usually with some sort of composition gasket and metal clamping device.

"Poly optic" technique. If two surface are ground and polished to an optically flat finish and are then brought into contact with each other, they will adhere, due to molecular attraction. If the two mating surfaces are absolutely flat, molecular diffusion will take place at room temperature and the glass parts will seal. Lesser degrees of flatness require greater

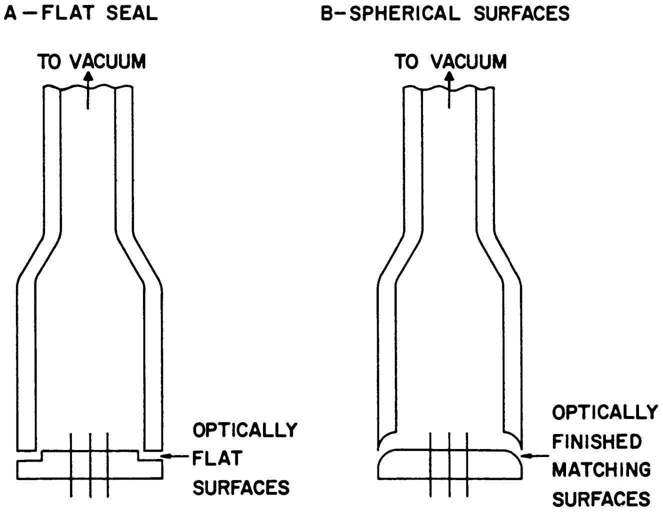


Figure 1
Poly-optic Seal

degrees of temperature to effect seals. This principle was first applied on a commercial basis by C. S. F. in Paris, France, during World War II. It has also been used in the United States by Chatam Electronics Corp.[1] The usual method employed in fabricating hermetically sealed tubes or enclosures by this technique, is to grind and polish the faces to be joined to a Johannson block-like finish, then align and press the two parts together and evacuate the tube. Atmospheric pressures will hold the two parts together until a seal can be effected. A variation of this process has been applied on a commercial basis by Allen B. Dumont Laboratories for sealing face plates onto the open funnel end of large television picture tubes.[2] In this method apparently used with a great deal of success, use is made of solder glass applied to the periphery of the quasi-optically polished surfaces to effect a strong and permanent seal. Wide use of the poly optic technique is limited by the fact that this is an expensive method of making seals. Costly machinery and skilled operators are needed to grind the glass parts to the degree of flatness required for effective sealing to occur. In addition, unless the finish on both mating parts is as good, or better, than that of a Johansson block, sealing will not occur at temperatures much below that at which glass softens.

However, even if the sealing takes place at a temperature close to that at which glass softens, this sealing method will still have merit, for the sealing temperature will be below that at which glass is worked in conventional flame sealing, also since the seal is normally made with the internal structure under vacuum, and since no combustion products enter the sealed off device, the internal structure of devices sealed in by this process tend to be cleaner and longer lived than those sealed in by conventional flame working methods.

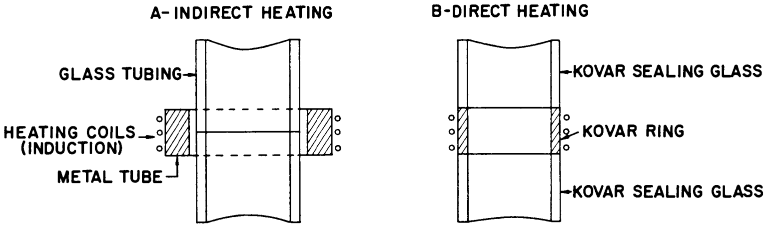


Figure 2
Electrical Heating

Electrical Heating. If glass is heated to its softening or working temperature and then brought into physical contact either with another piece of heated glass or with some other properly prepared and properly matched material, wetting and sealing will occur. Some methods of electrically heating glass for sealing purposes are as follows: *A.* Indirect heating (radiant heating). In this method a fixture such as a metal or graphite ring is placed in close proximity to the parts being joined and is then heated, either directly by resistance heating or by induction. This hot fixture, in turn heats the glass parts being joined by radiation causing them to soften so that sealing can take place. Fig. 2a

Although this method does not appreciably reduce the amount of heat required to effect a seal, it does have the advantage of eliminating the flame used in conventional sealing methods thereby eliminating any contamination which might be introduced by combustion products. *B.* Direct heating. An interesting variation of the above technique is to "sandwich" a conducting ring or disc, of an appropriate metal, (*i.e.* Kovar) between the two pieces of glass to be joined.[3] The metal, usually heated by induction, causes the glass surfaces, in contact with it, to soften. If the metal has been properly prepared, the softened glass will now adhere to it, effecting a seal. Many variations of this ring method have been successfully used, and can also be applied to making glass-to-metal seals. When glass is sealed by the interposition of a metal ring in this matter it is usually accomplished at a somewhat lower temperature than when sealed by direct heating, however, since these seals contain a glass-to-metal seal, they also contain a stressed area about that seal, so that cracking may occur more readily in this type of seal. Fig. 2b.

C. Arc Sealing. Another useful and interesting method of sealing glass is to use a high voltage electric arc. This method, developed by Corning Glass Works,[4] takes advantage of the electrical conductivity of the glass itself. This may seem strange, since most of us know glass as an insulator, as it is at room temperature, however, if the temperature of glass is raised its electrical resistance drops. If the temperature is raised high enough the glass will actually become a conductor. This characteristic is utilized for arc sealing by causing the glass to become hot enough to conduct electricity. When this happens the electric arc transfers from air to the lower resistance of the glass. The temperature of the glass rises very rapidly due to resistance heating; softens and can be sealed.

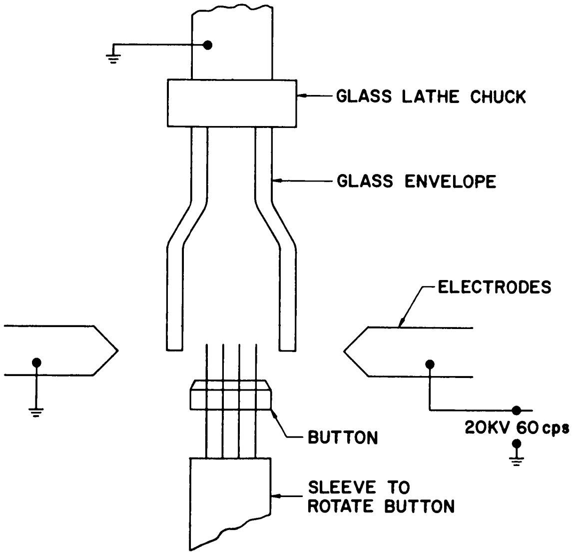


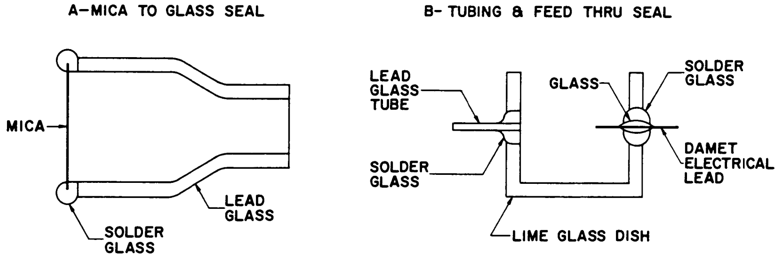
Figure 3
Arc Sealing

Two types of electrodes are in common usage in arc sealing, flame electrodes and solid electrodes. In using flame electrodes, the high voltages are actually applied to lighted gas burners. The flame supplying a copious source of ions, so that an arc may be struck in air at reduced voltages. Additional advantages of using flame electrodes are that the work may be pre-heated and, after sealing, annealed by the flame. This type of seal is usually used for large work and heats the glass parts being joined to a considerable degree. However, the seal area is highly localized and the joints made in this manner are usually strong and tight.

Solid electrodes are used, usually for hermetically sealing small glass tubes such as transistor enclosures where low temperatures must be maintained throughout the entire sealing operation. Operation is similar to that for the flame electrodes. The parts to be sealed *i.e.*, bulb and stem, are set in a glass lathe and carefully aligned so that the outer diameters of the parts to be sealed are concentric to each other, with the plane of the open end of the stem parallel to, and slightly inside the open end of the bulb. High voltage electrodes are then positioned in the plane of the open end of the bulb. The glass parts are set into rotation and an arc is struck in air. Radiation and "splash" of this arc heat the glass causing its electrical resistance to decrease. When this resistance is less than that of the air gap between the electrodes, the arc enters the glass and very rapid heating occurs so that the glass softens and can be sealed. Corning Glass Works has applied this sealing method to soft glass transistor enclosures so that a complete hermetic seal can be made in twenty seconds. The U.S. Army Signal Corps at Fort Monmouth has extended this method somewhat by applying arc sealing techniques to hard glasses and to somewhat larger electron tube bulbs and stems.[5]

To take full advantage of rapid sealing with a consequent minimum temperature rise of the bulb's sealed-in components, arc sealed bulbs are not annealed, for annealing would raise internal bulb temperatures above the desired levels. Lack of annealing seems to have no ill effect on small diameter tubes sealed in this manner. However, in the case of larger tubes, the strain may induce a great deal of shrinkage in the completed devices.

D. *Solder glass.* Next to the glassblower's art, perhaps the most useful and versatile glass working methods are those involving use of solder glass. Vitreous type of solder glass have been in common use for many years. They are low "melting" glasses which can be applied to higher "melting" glass at temperatures just below or just above their annealing temperatures to make a seal in a manner similar to that of soft soldering metal.


A–MICA TO GLASS SEAL

B– TUBING & FEED THRU SEAL

Figure 4
Solder Glass Seals

The devitrifying type of solder glass has become very popular since its introduction a few years ago, and several excellent papers on this subject have been published.[6,7] Its popularity is due mainly to the fact that after heat treatment it attains a permanent stability and can be reheated to temperatures even higher than the original sealing temperature with no deleterious effect on the seal. The extreme usefulness of these materials manifests itself by the fact that it is possible to make seals in places that would be either very difficult or impossible by conventional glass blowing techniques, *i.e.*, in our laboratory we have "sealed-in" buttons at the edge of CRT tube funnels by ultra-sonically drilling holes and solder glassing the buttons in place.

One very useful fact, is that glass bonded by this method can be released by soaking in hydrochloric acid. The parts can then be cleaned and re-solder-glassed.

Soldering techniques are not really low temperature methods of sealing glass since the glass must be raised to a rather high temperature in order for sealing to occur, approximately 430°C. for the soft glass solders and 600°C. for the hard glass solders. This is still considerably below the temperature at which glass is worked in a flame and the permanence and strength of the seals are comparable to flame worked glass. In addition this method offers the convenience of hermetically sealing glass to configurations difficult or impossible to attain by conventional flame working methods.

Use of Epoxy Resins—In the past few years phenomenal success has been achieved in making vacuum tight seals by the use of epoxy resins[7,8,9]. Strong hermetically tight seals can be made in this manner at temperatures of 100°C. to 200°C. Seals can be made at even lower temperatures by using greater amounts of catalyst when mixing the epoxy, or by using longer cure time.

Mr. George Horky[10] of Special Techniques at this laboratory has successfully used epoxy cements to bond "quartz" (fused silica) windows to Corning 7740 glass, 7740 windows to monel tubing, "quartz" to copper, 7740 to brass, kovar to quartz, kovar to 7740 glass, quartz to quartz, and 7740 to 7740.* These seals were found to be hermetically tight when helium leak tested at 5.3 x 10^{-10} cc/sec. Windows made by this process for cryogenic work have been used at liquid helium temperatures and found to still be vacuum tight after four months of use. A final check of this work here was made by sealing a "quartz" window to a 7740 tube and then fusing an ionization gage onto this tube. This assembly was exhausted and baked at 120°C. for twelve hours and then "tipped off". Measurements made on the ion gauge read 2.8 x 10^{-7} torr. This same pressure was read again one week later. Of course, pumping by the ion gauge itself could have masked a somewhat high pressure, but the test does prove that a seal made in this manner is really vacuum tight.

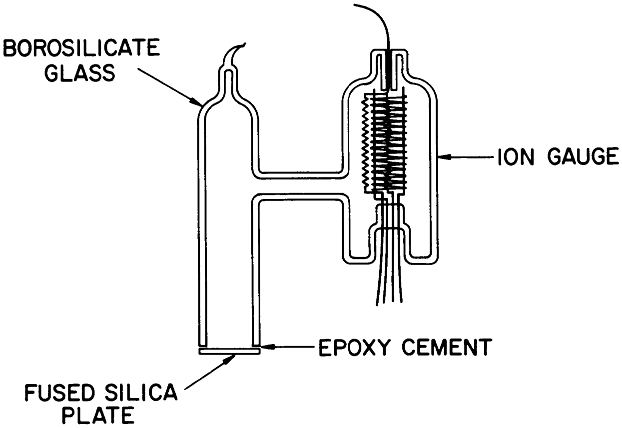


Figure 5
Epoxy Seal

The method used here for making the seals was as follows: Plastic Associates epoxy #708F and 708F catalyst were used in the ratio of two

---

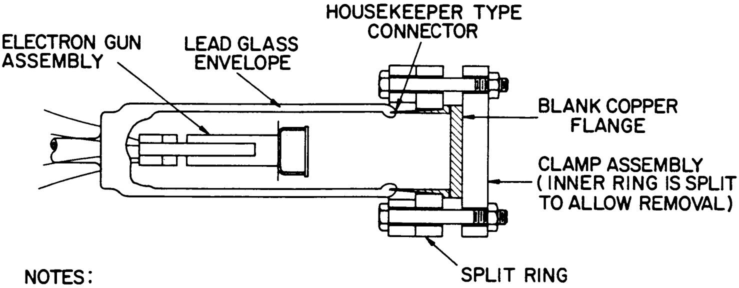
*The "quartz" referred to above is the fused silica commonly called quartz by glassblowers.

parts of resin to one part of catalyst, Corning Solder Glass #7574 in the form of a powder was used as a binder. It is felt that use of such a binder will help change the coefficient of expansion of the epoxy to more nearly match that of the glass used.

A typical formulation of the mixture is:

708-F Resin — 8 grams
708-F Catalyst — 4 grams
#7574 Glass powder — 20 grams.

Epoxy bonded seals are strong, easily fabricated, hold up well in use, and can be made to a variety of shapes. However, they cannot be baked at really high temperatures and the epoxy will outgas, especially if it has not been cured sufficiently. In all, however, this is a very useful and convenient sealing method.



NOTES:
1. CLAMP ASSEMBLY IS USED ONLY DURING BONDING OF JOINT.
2. ELECTRON GUN ASSEMBLY IS SEALED TO ENVELOPE ONLY AFTER BONDING IS COMPLETED.

Figure 6
Thermal Compression Bond

Thermocompression Bond. If two clean, accurately machined surfaces are gold plated, or separated by a thin gold foil and then pressed together at a moderate temperature, well below the melting point of gold, a so called diffusion seal or thermocompression bond may be effected[11]. This seal is especially useful in joining accurately machined metal parts, preferably copper or brass since copper bonds so well to gold. Mr. E. J. Taschler of the Special Techniques Group in this laboratory, has applied the idea of thermocompression bonding to a low temperature sealing-in method for glass. A specially designed flange of OFHC copper was sealed to glass using a Houskeeper seal. The flange was then plated first with nickel using the electroless method and then with gold using temperex H.D. gold solution. 0.0005″ of gold was plated onto the flange; this type of plating permits the plated part to be heated to 500°C. in air without showing any detrimental effects. This part was then clamped to a similar flange and the assembly slowly brought up to a temperature of 450°C. After slowly cooling to room temperature it was found to be hermetically tight when tested with a mass spectrometer leak detector.

No doubt, many other methods of attaining the results discussed above, exist. It is hoped that some day a complete compilation of these methods will be made. In the meantime, perhaps, this paper may serve the experimentalist to choose some sealing method best suited for his purposes.

BIBLIOGRAPHY

1. "Industrial Preparedness Study on Low Temperature Sealing (Poly-optics) of Tubes."—*First Quarterly Type Progress Report,* Period of June 29, 1956 to March 11, 1957. Signal Corps Contract DA-36-039-SC72700—Signal Corps Order 50809, Philadelphia 56-81.

   Placed by: The Army Signal Corps Supply Agency.

   Contractor: Chatam Electronics.
2. "A Quasi-Optical Seal for Vacuum Tubes" by M. P. Wilder—Allen B. Dumont Laboratories. *Proceedings of the Fourth National Conference on Tube Techniques.* (New York University Press.)
3. U. S. Patent No. 2,568,466 Nolte of G. E.
4. U.S. Patent No. 2,306,054 E. M. Guyer of Corning Glass Works.
5. "Arc Sealing in Borosilicate Glass by Morris Liebson. *Materials and Electron Device Processing ASTM Special Technical Publication No.* 300.
6. "The Use of Devitrifiable Solder Glass in Experimental Vacuum Devices by K. D. Early and D. E. George. *Proceedings—The Sixth Symposium on the Art of Glass Blowing.* Published by: American Scientific Glassblower's Society, Wilmington, Delaware.
7. "A Solder Glass Sealed Vacuum Envelope to Operate at 500°C. Ambient Temperature" by Hilmar M. Heyn and Kenneth L. Rohrer. *Ibid.*
8. "Epoxy Resin as a Material for Constructing Cryogenic Apparatus" by R. G. Netzel and J. R. Dillinger, *Review of Scientific Instruments,* July 1961, Vol. 32, No. 7.

   "New Method of Sealing Infrared Window Materials to Glass" by Dowell E. Martz. *Review of Scientific Instruments,* Feb. 1961; Vol. 32, No. 2.
9. "Epoxy Joints for Sealed Off, High Vacuum Tubes" by J. F. Sayers, *Journal of Scientific Instruments,* Vol. 37, June 1960.
10. "Epoxy Bonding of Quartz Windows to Pyrex Tubing" by G. Horky, *IBM Research Note NC-232,* July 10, 1962 Proj. 4802.
11. *Tube Laboratory Manual,* Second Edition, p. 62-Research Laboratory of Electronics, M.I.T., Cambridge, Massachusetts.

THE FLAME SPRAY PROCESS AND SPRAYING TECHNIQUES

F. J. Dittrich
Metco Inc.
Westbury, Long Island, N. Y.

HISTORICAL:

Much of our modern flame spray equipment and technique has evolved from the original equipment and process developed in Switzerland by Mr. M. U. Schoop in the early 1900's. In 1882, a process for making lead powder by passing a stream of molten lead through a gaseous blast was patented in Germany. Schoop conceived the idea of preparing a metal coating by placing the article to be coated directly in the path of this atomized metal. As early as 1902, a process for producing a metal coating by impacting metal dust upon a base by means of a blast of unheated gas was patented, but this method was never used commercially. A United States patent, issued some years later to Mr. Schoop, disclosed a modification of this process in which ignited gases were used to melt and propel the metal particles to the substrate. Around 1910, a successful metallizing unit which atomized a stream of molten metal was developed, but this equipment was so massive that it seriously handicapped commercialization of the process.

The use of metal in the form of wire for spraying was first proposed around 1905, and in 1910 a metallizing "pistol" using an oxy-acetylene flame to melt the wire was designed.

An electric arc, struck between 2 identical wires to be melted, was used as a heat source in some of the early equipment, but this type of equipment was found extremely difficult to use because of two electrically "hot" wires required, and because of excessive oxidation of the materials as they were melted in the electric arc and propelled to the substrate by means of a compressed air blast. Use of this type of flame spray equipment is still in limited use, principally in Europe, today.

The wire metallizing process was first introduced into this Country in about 1920 when the original wire type Schoop gun was imported. The relative simplicity and ease of operation of this wire type equipment stimulated use of the process and the development of more reliable equipment. Wire spraying is by far the most widely used method of depositing metal coatings with the "metallizing" or "flame-spraying" process today.

The invention of the original powder spray equipment in which the powder materials are suspended in air, carried through a flame for melting, and propelled to the base by compressed air is generally credited to Shori, and is the subject of a British patent. This type of metallizing equipment has been in use for many years, but generally is restricted to spraying low melting point materials such as zinc or aluminum. The equipment, however, is not limited to these materials and excellent coatings of steels and bronzes can be deposited by this method. The wire process is used if possible because it is basically cheaper and faster.

The molten metal process, in which the metal to be sprayed is melted in a crucible and then atomized, is usually restricted to the spraying of very low melting point materials such as lead, tin, bismuth, or their alloys.

The airless chemical-flame powder-spray equipment, invented by A. P. Shepard and F. J. Dittrich, was introduced early in 1956. This process permits the spraying of practically any material, in powder form, with a melting point up to around 5000°F. The material to be sprayed is carried into the flame by a portion of one of the gases used to produce the heat for melting, and is propelled to the substrate by the products of combustion. This equipment is noted for its extremely high thermal efficiency. Spray speeds are fairly high and deposit efficiencies, with most material, are around 95%.

The plasma flame process was first introduced around 1958. Spray speeds and deposit efficiencies were low with the original equipment, therefore it was primarily used in laboratories for experimental work and not accepted for general use in flame spraying. The equipment and spray techniques have been considerably improved since that time, as we shall see later.

SUBSTRATE PREPARATION:

Regardless of the method used for melting and propelling the coating material to the substrate, proper preparation of the substrate surface is required in order to securely bond the flame-sprayed coating. Prior to the development of "self-bonding" coating materials, substrate preparation was accomplished either by grit blasting the surface or by machining preparation. Grit blasting serves a dual purpose in that the surface is both cleaned and roughened in a single operation. It is, however, necessary to remove all oil and grease from the substrate surface prior to grit blasting. With this method, all oxide films are removed from the surface, the surface is roughened and raised portions of the substrate surface are peaned over to provide undercuts into which the molten coating particles may key. This type of bond is almost entirely mechanical in nature although chemical and/or solid state bonding might also be involved. The entire mechanism of this type of bonding is not very well understood. Grit blasting results in compressive stresses in the surface layers of the substrate which tend to warp the surfaces. The stresses due to grit blasting can usually be ignored when massive bodies are prepared in this manner, but structures consisting of thin sheet elements can be warped beyond usefulness.

Machine element work can generally be prepared by rough threading, grooving and roughening with a special knurling tool, by grit blasting, or by using a self bonding bond coat. Rough threading is accomplished by cutting a full depth thread in one pass with a tool deliberately ground to produce a rough, ragged thread surface. Grit blasting can be used after the surface to be coated has been undercut sufficiently to allow the thickness of overlay required, and to provide a clean surface. An undercut surface on machine elements can be grooved and roughened using a special knurling tool previously mentioned, and this method provides one of the strongest mechanical bonds in use today.

The need for improved surface preparation methods has resulted in the development of "self-bonding" bond coats for subsequently applied flame sprayed coatings. Self-bonding materials are those which, when flame sprayed, will adhere strongly to a smooth surface. These materials require only that all contaminates and heavy surface oxide films be removed in order for particles in the spray stream to form metallurgical bonds on impact with the base. Mechanical keying is not involved in this type of bonding; high strength bonds are produced on surfaces polished, for example, to about a 4 microinch finish. Post-deposition heat treatment is not required to effect or to improve the bond. Surface oxide films can be removed by grinding, chemical etching (so long as no residue is left on the surface by the etchant), abraiding with very fine abrasives such as aluminum oxide at low air pressures, or abraiding the surface with fine, clean emery cloth. Coatings can be applied to hard, brittle base materials, which cannot be prepared by grit blasting, by using a self-bonding bondcoat to provide the adhesion for the desired coating material. In addition, thin sheet structures or tubing can be coated without danger of warping due to grit blasting.

There are a number of metals which, when flame sprayed, are self bonding to some base materials under certain conditions. Molybdenum self-bonding was developed by A. P. Shepard in 1947. Except for molybdenum, none of these is in common use today because of special atmosphere, temperature control, cost, or other requirements which make them impractical for general use. Molybdenum is the most commonly used self bonding material, and is used as a primary coating for its own particular attributes such as wear resistance, or as a thin bond coat for other coatings. Use of molybdenum is restricted in high temperature oxidizing atmospheres by its high oxidation rate at temperatures over approximately 600°F., and the volatility of its oxides at high temperatures. Used as bond coat, molybdenum is sprayed on to a clean substrate surface in thicknesses ranging between .002″ and .005″, the as-sprayed surface of the molybdenum coating providing the desired roughness of coating to which other materials can mechanically bond.

More recently, in April of 1963, a completely new self-bonding material—nickel aluminide—was introduced to users of the flame-sprayed processes. This unique material is a powder in which each particle is a core of aluminum clad with a coating of nickel which may be sprayed with either combustion or plasma flame equipment. Immediately upon entering the flame, each particle is raised to its "ignition" temperature, an exothermic combination reaction is initiated, the nickel aluminides are formed, and considerable heat is generated. "Ignition" is used to describe the initiation of the combination reaction—it should be understood that no combustion is involved; the combination reaction does not require and is not supported by oxygen. The continuation of the exothermic combination reaction can be observed visually in the flame. High speed motion pictures, taken at 8000 frames per second, showed the individual particles glowing more brightly as their temperature increased as they traveled further from the nozzle, away from the hottest zone of the combustion flame. This is in contrast to spraying the conventional powder materials where particles reach peak temperature in the hottest part of the flame, and then cool during travel away from the nozzle. The nickel aluminide coatings deposited are self-bonding to the smooth surfaces of many substrate materials including annealed or hardened carbon and alloy steels, cast irons, the stainless steels, nitrided steel surfaces, aluminum, titanium, tantalum, columbium and columbium alloys, cobalt, various glass formulations, quartz, and graphite. Flame sprayed nickel aluminide coatings are an improvement over flame sprayed molybdenum coatings for bonding because they are more consistent in strength and have higher strength. In addition, the nickel aluminide coatings in themselves are oxidation resistant to temperatures around 2000°F. This new coating material is finding wide useage in nearly every industry.

Bonding flame sprayed coatings to brittle substrate materials such as, cast iron, hardened steel, glass or ceramics can be a difficult procedure. It is impossible to prepare these substrates using the usual grit-blasting preparation techniques. Generally, the surfaces can be roughened somewhat by blasting with unabrasive grit, such as boron carbide or aluminum oxide, whose particle hardness is greater than that of the material to be prepared. The formation of the "undercuts" and "keys" which are vital to the adhesion of the applied coating, is impossible due to the brittle nature of these particular materials.

Bonding to cast iron or to hardened steel substrates can be easily accomplished using one of the self bonding materials, previously described, as an intermediate coating to provide adhesion for the desired coating material.

Bonding to most glass surfaces, or to porous, unglazed ceramic surfaces, can also be easily accomplished with most metal coatings. Most glass substrates can be coated by first removing all surface contamination by solvent wash, preheating the substrate, and then spraying with aluminum, zinc, copper or copper alloy, or tin, to mention a few metals. Spraying higher melting point, less ductile, metals such as nickel aluminide, steel, or molybdenum for example, directly onto glass surfaces may produce a crack pattern on the glass surface due to extreme thermal shock and/or thermal expansion mismatch. The deposited coating generally separates from the substrate by pulling particles of glass out of the coated surface. This condition has been eliminated in the past by first spraying an undercoat of zinc or aluminum and then overcoating with the desired material.

Bonding to high sintered, high density, high melting point ceramic substrates presents more and different problems. Obviously, even grit blasting with boron carbide can do no more than slightly roughen these substrate surfaces. Most metals will not "wet", and therefore become self-bonding; the lack of bond and high thermal shrink of most metals results in cracking of the metal overlay and complete loss of the coating. Bodies of Al_2O_3, sintered to nearly maximum theoretical density, may be coated by plasma flame spraying tungsten onto a previously cleaned surface. The tungsten may be used as the primary coating material, or may be used as a bond coat for other more desirable metal overlays. The nature of the bond has not been investigated, nor has the strength of the bond been accurately determined as yet. There are probably other metals, such as molybdenum or alloys of molybdenum, which could produce the same bonding effect.

Glass, sprayed with airless chemical flame powder spray equipment will bond to most ceramic, or other glass, materials. The substrate surface must be clean, preheated, and the glass overlay applied so that it fuses as it is deposited. Thermal expansion rates of substrate and coating must, of course, be quite closely matched.

GENERAL PROPERTIES OF FLAME SPRAYED COATINGS:

Flame sprayed metals are new metallurgical materials with physical properties entirely different from the original metal sprayed. In general, flame sprayed metal coatings are harder, more brittle, and more porous than the original material. Higher hardness can be due to the radical quench from approximately the melting point of the metal to the substrate temperature, usually less than 300°F., and to the inclusion of a small percentage of oxides which form on the particles in spraying. Porosity is inherent in the process and varies with the material sprayed, and the type of equipment and/or spray parameters used. It can range from a low of approximately ½% to a high of 20% or more, if it is so desired. Flame-sprayed machine-element bearing surfaces show reduced wear when compared to surfaces of conventional materials because of high particle hardness and the oil retained in the pores in the coatings; this is comparable to oil retention in the pores of pressed and sintered porous powder-metallurgy bearings.

A relatively new kind of flame sprayed coating is that in which a metal alloy, usually a Nickel-Chromium-Boron-Silicon alloy, is deposited on the surface and fused after deposition to form a hard, non-porous overlay which is fused to the substrate surface. One of the softer alloys of this class of materials is used on glass mold plungers to resist oxidation, attack by molten glass, and cracking due to thermal shock. This type of coating is most useful in applications where heavy wear and/or abrasion resistant coatings are required. Tungsten carbide particles, usually cobalt bonded tungsten carbide composite grains, are blended with this type of self-fluxing alloy material to resist extremely heavy wear and abrasion.

Ceramic coatings, applied by (1) the chemical flame powder spray process (2) the plasma-flame powder spray process, or (3) the rod spray process, again, are new engineering materials whose physical properties are very similar to the flame sprayed metals. The coatings are brittle and porous, and in addition adhesion to some grit blasted substrate surfaces as poor unless an intermediate bond coat of an oxidation resistant material, such as a nickel-chrome alloy, is first deposited on the grit blasted surface. The ceramic will bond more strongly to the as-sprayed surface of the undercoat than it will to the roughened surface of most substrates. Porosity and hardness of ceramic coatings are dependent on the material sprayed, the equipment it is sprayed with, and the spray parameters used with each of the 3 basic types of equipment. Porosity can be varied, for almost any given material, from less than .5% to more than 20%, if it is desired, by simply varying spray parameters such as material feed rate through the flame, spray distance between gun and substrate, particle velocity on impact with the substrate, particle size range of the starting material, be it powder for spraying or the starting powder from which rods are fabricated. With the rod spray process, texture (or smoothness) of the deposited coating also appears to vary with the size of the powder particles from which the rods are fabricated. Hardness and abrasion resistance vary almost directly with porosity in ceramic coatings and can be varied in much the same manner as can porosity.

Thermal shock resistance of ceramic coatings, resistance to separation from the substrate due to thermal cycling and mismatch of thermal expansion rates between coating and substrate, for a given coating material, varies with the bond strength of the coating to the substrate and the porosity of the coating. The more porous the coating is, the less susceptible it is to separation from the substrate in thermal cycling. The higher the bond strength, the denser the coating that will resist separation from the base in thermal cycling. However, as maximum theoretical density of the ceramic coating is approached, the danger of separation due to thermal cycling and the radical differences between ceramic coating and the usual metal substrates substantially increases, regardless of the bond strength. Just as fused glass coatings on steel substrates will fail by spalling if the thermal expansion rates of coating and substrate are not closely matched, so will flame sprayed ceramic coatings fail if maximum theoretical density is approached too closely.

A hard Al_2O_3 coating of some considerable thickness deposited on a grit blasted 300 series stainless steel surface will have low bond strength and will easily separate from the substrate, often in cooling to room temperature after coating. Application of a "bond coat" of nickel-chrome alloy, .003" to .005" thick to the same substrate prior to deposition of the ceramic coating will improve bond strength so that the resultant coating system can be thermally cycled to some extent without loss of bond.

Thermal shock resistance of ceramic coatings can be markedly improved through use of cermets or cermet coating systems. Mixtures of metal and ceramic powders in various proportions have been flame sprayed to form layered coating systems. The layers closest to the substrate are richer in the metal phase, which is gradually decreased until the surface layer is 100% ceramic. Coating systems such as this have withstood repeated thermal cycling in plasma flame materials evaluation facilities in several laboratories, including an Aeronautical Systems Division Program. (WADD) A mixture of 40 wt. % of the nickel aluminide powder previously mentioned and 60 wt. % of Al_2O_3, sprayed approximately .020" thick on a low carbon steel panel 1" x 3" x 1/8" successfully withstood 10 cycles of heating to over 1800°F. in an oxy-acetylene torch flame and quenching in room temperature water.

WIRE AND ROD SPRAYING:

Modern wire and rod spraying equipment bears little resemblance to Schoop's original "pistol". The original equipment was difficult to light, difficult to adjust for proper spray conditions, and even more difficult to keep operating for extended periods of time without backfire or other malfunction. Continuous research over the last thirty years has resulted in the development of wire and rod spraying equipment which are simple to use, reliable in operation, may be used continuously in production applications, and deposit materials many times faster than the original equipment could. Governed air turbines have resulted in consistent wire feed rates which remarkably improve the consistency of the deposited coatings. Wire or rod speed in the modern units can be varied in stepless increments so that practically any material that can be formed into wire or rod can be sprayed. Electronic speed control of electric drive motors has resulted in very stable wire and rod feed rates from a low of several inches a minute required for spraying ¼″ diameter ceramic rod to over 30 feet per minute required for spraying low melting point metals.

Siphon-jet gas metering systems and mixers have resulted in precise and consistent flow of all the gases used in our equipment today.

"Push-button", or completely automated, flame spraying has been a reality for several years. Heavy duty flame spray guns for metals and ceramic rods, completely controlled by an electronic console through all steps required for their operation, are in use in production applications. Some of these units have been tied in with other basic machinery, in line, so that the flame spray gun will start up and operate on signal from a main production line control. On activation, the unit will cycle through gas line purge, reduction to gas ignition flow rate, ignition, full run gas flows, and activation of the flame-out detector. Accidental flame-out or decrease in gas supply pressures to less than a present minimum will automatically shut down the entire unit. Wire feed can be controlled from a remote station or by push-button control on the console.

Equipment for spraying ceramic rods is almost identical to that used for spraying metals in wire form. The main difference is in the rod feed system which must maintain precise speed control from a low of about 3″/minute to approximately 15″/minute maximum instead of the 1.5 to 30 ft./minute required for metal wire.

When the ceramic rod spray process was first announced, a little over 8 years ago, only Al_2O_3 rods in ⅛″ diameter were readily available for spraying, and zirconia rods ⅛″ in diameter were emerging from the laboratory. Announced spray rates at that time were around .5 lb. per hour material sprayed at approximately 50% deposit efficiency. Continuous improvement in rod spray equipment has resulted in radically increased spray speeds and thermal efficiency so that it is now possible to spray approximately 3 lb./hour of Al_2O_3 at about 78% deposit efficiency or approximately 2 lb./hour of ZrO_2 at about 60% deposit efficiency. Part of the increase is due to the increase in rod diameter used—now ¼″ instead of the original ⅛″ diameter.

Efforts to increase spray rate and improve the quality of coatings are continuing. One of the latest innovations is a ¼″ diameter zirconia rod with 8 radial slots approximately .010″ wide and approximately 3/64″ deep formed in the surface of the rod. The objective of this change is to present more surface area to the flame to improve heat transfer to the rod. This is accomplished, and spray speed is increased around 25% to approximately 2.7 lb./hr. The deposited coatings are somewhat coarser than when solid rod is used.

Ceramic coatings deposited using the rod spray process are dense, hard, and abrasion resistant with good bond strength. Coating texture using ¼″ diameter rods is only slightly coarser than that produced using ⅛″ diameter rods; all other properties remain essentially the same. Ceramic rods of alumina, zirconia, zircon, chromium oxide, and a magnesia-alumina spinel are now readily available. The process is not as versatile as the powder spray processes, since rods must be fabricated. This can be a costly and time consuming operation.

Alumina and zirconia coatings deposited using the rod spray process are very widely used in a great variety of applications in which their main attributes—wear and abrasion resistance, high melting point, and low thermal conductivity—are effectively used. A great many of the combustion chambers, throats, and exit cones of rocket and missile engines in use today have been lined with alumina or zirconia using the rod spray process. Pump plungers, for instance, for use under highly abrasive and/or corrosive conditions are flame sprayed with Al_2O_3 quite successfully.

The rod process has a number of disadvantages, among which are slow spray speed, low deposit efficiency, and rod-ends which spit out during spraying, which may adhere to the work.

It is usually not practical to deposit glass coatings using glass rods and the rod spray process. While the equipment is capable of feeding and melting any glass rod, the resultant "sprayed" material is usually a glass "wool". Instead of atomizing into minute droplets, small diameter fibres form, and cool rapidly because of the quenching effect of the compressed air envelope surrounding the flame and entry into the cooler air atmosphere. The fibres may be collected with suitable equipment; small quantities of quartz "wool" have been manufactured in this manner by spraying quartz rods.

THE CHEMICAL FLAME POWDER SPRAY PROCESS:

There are two basic types of chemical-flame powder spray equipment.

The first is the Schori-type equipment in which the powder to be sprayed is picked up in an aspirating jet of air and conveyed through the center of a concentric ring of jets in a nozzle through which the combustible mixture of acetylene and oxygen emerge. The nozzle is surrounded by a concentric shield of compressed air which cools the burner and aids in propelling the molten particles to the substrate surface. The powder carrying air conveys the particles through the flame at fairly high velocity and, in addition, dilutes and cools the flame. This combination of high particle velocity and cooler flame permits the spraying of low melting point metals such as lead, tin, zinc, and aluminum. Self-fluxing, hard facing alloys with melting points around 1950°F. and bronzes and steels can also be sprayed with this type equipment. The coatings deposited are almost identical to those deposited using the wire spray process. Spray speeds are generally somewhat slower, but in some cases deposit efficiencies are higher than with wire. Neither the higher melting point refractory metals such as molybdenum, tungsten, tantalum, etc., nor the higher melting point refractory ceramics such as oxides, nitrides, borides, carbides, etc., can be effectively sprayed with this type of equipment.

The second basic type of chemical flame powder spray equipment is known as ThermoSpray and uses no compressed air at all either to convey the powder or to aid in propelling the melted particles to the substrate. Introduced early in 1956, this type of equipment probably has the highest thermal efficiency of any chemical-flame spray unit. The powder to be sprayed is gravity fed through a metering orifice into an aspirator where the powder is picked up by a small portion of one of the gases used to supply the heat for melting. This is usually the combustible gas, either acetylene or hydrogen. In spraying the metals which melt below approximately 3500°F., the powder is carried through a single axial port into the center of a concentric ring of parallel axial mixed gas jets. These form a ring of flame surrounding the particles, into which the particles diffuse as they are propelled to the substrate.

In spraying materials which melt over approximately 3500°F., the method of feeding and carrying the powder particles is identical. However, for these materials a special nozzle splits the axial-flowing stream of carrier gas and powder particles into a number of smaller streams, each flowing angularly away from the axis of the nozzle in a radial pattern. Each of these streams is injected into a jet of burning gas where the particles are intimately mixed with the flame, heated to over their M.P., and propelled to the substrate surface.

The lower melting point metals, tin, lead, cadmium, zinc, or their alloys cannot be sprayed with airless chemical flame equipment without extensive modifications, all of which result in reducing the flame temperature and/or increasing the particle speed through the flame. The metals which melt in the approximately 1200°F. to 2000°F. range, with the notable exception of the self-fluxing hard-facing alloys, are best sprayed, with this equipment, using a hydrogen-oxygen rather than an acetylene-oxygen flame. The self-fluxing hard-facing alloys which melt in the 1850°F. to 1950°F. temperature range and all other materials which have melting points over approximately 2000°F. may be sprayed with the airless acetylene-oxygen flame.

The high flame temperature and thermal efficiency of this type of equipment permits the deposition of excellent coatings of metals with melting points up to and including that of tantalum, which is about 5490°F. (±90°F.), and of ceramic materials with melting points up to and including that of zirconia, which is just over 4700°F. The high thermal efficiency results in relatively high spray speeds and in extremely high deposit efficiencies. Self-fluxing hard facing alloys can be sprayed at 15 lbs./hr. at 96% deposit efficiency. Al_2O_3 can be consistently sprayed at 3¼ lbs./hr. at 96.5% deposit efficiency and ZrO_2 can be sprayed at 2¼ lbs./hr. at 80 to 85% deposit efficiency, compared to 60% D.E. for ZrO_2 rod.

Spray speed and deposit efficiency are extremely important when comparing the economics of the various flame spray techniques. Costs of spraying, that is gases, labor, and overhead generally are fixed expenses. High thermal efficiency in the spray unit results in high spray speeds, which reduces the cost per pound of material sprayed. High deposit efficiency materially reduces the cost per lb. of material deposited by eliminating waste. When you consider that many materials being commonly sprayed cost over $10/lb., a high deposit efficiency is indeed important.

Conventional air-feed chemical-flame powder spray equipment could be used for depositing some glasses in powder form, particularly those with lower softening temperatures. The air shield around the flame and the air powder-carrier gas which dilute the flame and permit the spraying of lower melting point metals would tend to lower the maximum softening point glass sprayable with this type of gun. The airless types of chemical-flame powder-spray equipment is not restricted in that manner; practically any glass in powder form may be sprayed. Even the high lead glasses with their lower softening points have been sprayed using precautions to protect the operator and the area around him. This precaution is required with toxic materials regardless of the type of equipment being used.

Glass coatings may be flame sprayed onto metal substrates using either of two techniques. With the first, the substrate is grit blasted, preheated to 250°F.-350°F., the glass sprayed on and subsequently fused. With the second technique, only removal of surface contamination is required. After cleaning, the substrate is preheated to a temperature at which oxide films form. The glass is then sprayed on and fused as it is applied.

Plasma flame equipment, to be described later, may be used instead of the airless chemical flame equipment for depositing glass coatings. The same spray techniques are used with both methods, and the coatings deposited are of essentially the same quality.

Although flame spraying offers a means of producing glass coatings, there are actually not very many applications in use. There are several reasons including the usual problem of matching co-efficient of expansion of coating and base; probably not enough effort has gone into solving this type of problem for the case of flame spraying. Since each individual case or application is different, the type of glass chosen for a job depends on the particular situation. Experience has shown that this often requires testing of many different glasses for a particular application, and this generally means joint efforts between those experienced with the glass industry and those familiar with flame spraying.

The inherent simplicity of this type of equipment and the spray techniques required, and the fact that readily available powders can be sprayed make this the most versatile of all the chemical flame spray equipment.

PLASMA FLAME SPRAY EQUIPMENT:

The newest technique and equipment for flame spraying—the plasma flame—is probably the most versatile of all at this time and probably has the most potential for future use, barring any radical break-through in chemical flame equipment.

The heat source is a D.C. electric arc of high intensity, struck usually between a water-cooled tungsten electrode and a water-cooled copper nozzle. The direct current is supplied from a rectifier type power supply unit, power for which is supplied through alternating current mains. The most common equipment is conservatively rated for continuous operation at D.C. power levels up to approximately 40 kilowatts, but for intermitten operation, much higher power levels are possible.

The plasma gas is used as a carrier to transfer heat available in the arc to the particles of material to be sprayed. A primary gas such as Argon, Nitrogen, or Helium is brought to a control unit under regulated pressure. In some types of equipment, the primary gas is mixed with a secondary gas, usually around 15% hydrogen by volume, which is also brought to the control unit under regulated pressure. The gas proportions are precisely regulated and the total flow of gas accurately controlled by valves and flow meters in the control unit. The temperature and heat content of the plasma gas is controlled by regulating the arc current, the flow of plasma gas, the choice of primary and secondary gas and their proportions, and by selection of a proper nozzle.

Hydrogen, as previously mentioned, is the usual choice of a secondary gas, where one is used, for several reasons. It raises the voltage of the arc and thus permits the use of higher power; it burns with atmospheric oxygen to give additional protection from oxygen to the material being sprayed, and increases the heating efficiency of both the plasma and the articles being sprayed.

The powdered material to be sprayed is supplied in accurately metered quantities by a powder feed unit, usually carried by a gas stream taken from the supply of primary plasma gas. Introduced into the plasma downstream of the arc, the particles are melted and propelled to the substrate as molten droplets by the plasma stream as it flows out through the nozzle orifice.

Plasmas have proved to be superior to the classical relatively un-ionized gases when used as heat exchange mediums. The fundamental reason is that in the gas of a plasma there is at least one important state-change through which the gas passes to become ionized plasma. When it passes through this state-change, it absorbs heat without a very large temperature increase. Conversely, when it is being used as a heating fluid it delivers this heat of state-change without reducing the temperature very much. The fact becomes particularly important where the surface to be heated is that of a small particle of material propelled by that gas. The very fact that the gas is propelling the particle makes it difficult to obtain the high "wiping" difference between gas velocity and particle velocity, which is required for efficient heat transfer between a hot, classical, relatively un-ionized gas and a surface to be heated.

Nitrogen is the usual choice for the primary plasma gas, although argon is quite commonly used and helium may also be used. Diatomic gases such as nitrogen and hydrogen pass through at least two substantial state-changes when energized. They are first disassociated from molecular gases into atomic gases by separating the atoms of the molecules, and then ionized. In principle, therefore, diatomic gases make fundamentally better plasmas for heating purposes than monatomic gases such as argon or helium which pass through only one substantial state change in the arc, ionization.

Besides high heat content, the plasma gas must also have sufficient density to accelerate the particles sufficiently to give high impact velocities on the substrate to form dense coatings. For this reason too, the denser nitrogen is superior for general purpose spraying. The plasma gas is also required to protect the sprayed material from undesired chemical reaction. Nitrogen mixed with 5% to 25% hydrogen has proved to be satisfactory for protection from atmospheric oxygen. In this respect, the mixture is better than argon or helium unless additional shrouding or an inert gas atmosphere chamber is used. The hydrogen in the mixture burns with the atmospheric oxygen which diffuses into the plasma stream and thus gives more protection than an inert gas. Obviously, nitrogen cannot be used where the chemical action of the nitrogen is detrimental to the coating. Actual experience shows, however, that theoretical predictions in this regard are not very reliable. This is because the exact time-temperature conditions for nitriding are not very well known, and also because the effects of small quantities of nitrides included in the coating are not necessarily detrimental. For instance, while nitrogen has not been found most satisfactory as a plasma gas for spraying the various carbides, it is quite satisfactory for spraying tungsten for most applications. In fact, nitrogen sprayed tungsten coatings generally have better physical properties, such as density, than argon sprayed tungsten. It is possible that the better properties of nitrogen in this case more than offset any possible disadvantage of nitride content. Even columbium and tantalum metals can be sprayed better with nitrogen using a nitrogen shroud than with argon using an argon shroud.

Argon is the most chemically inert gas commercially available and, for all practical purposes, may be considered completely inert for flame spraying purposes. As previously stated, however, it is a much poorer heating medium than nitrogen. There are some materials, such as the carbides and silicides, which are adversely affected chemically by nitrogen but which can be satisfactorily sprayed using argon. The usefulness of argon for spraying such chemically active materials is seriously reduced by oxidation and nitriding by atmospheric air which is aspirated or diffuses into the plasma stream. Unless additional protection is provided by shrouding the entire operation with additional argon, or spraying in an enclosed chamber using argon atmosphere, its value as a plasma gas is much diminished.

Helium does not appear to offer much promise for flame spraying, although some equipment has been designed to operate with this gas. Although it is highly inert to most substances, it is not as inert as argon. Helium does not have the reducing properties of hydrogen, has the relatively poor heating properties of the monatomic gases, and also has low density. However, it may be used in the laboratory where there is a chemical reason for doing so.

The choice of plasma gas is not an important factor in determining heat contribution to the substrate. No matter which gas is used, the heating of the substrate will depend almost entirely on (1) the kind and rate of material being deposited, (2) the heat output of the plasma flame spray gun as determined by the number of watts of power consumed, and (3) the distance of the gun from the work.

At the present state of the art, the plasma flame technique probably has the highest potential for maximum spray rate, maximum deposit efficiency, consistency in quality of deposited coatings, and versatility in the range of refractory metal and ceramic materials that can be sprayed. Extremely hard, dense coatings of Al_2O_3 can be deposited at the rate of 4 lbs/hr or better. In a developmental setup now being field tested, zirconia is being sprayed at the rate of 14 lbs/hr with a deposit efficiency of 80 to 85%. This is approximately 5 times faster than any chemical flame equipment can presently spray this material.

The ability of the plasma flame system to spray materials with melting points over approximately 5000°F. puts it in a class by itself as far as these materials are concerned. Tungsten, for instance, can be sprayed using the plasma flame technique, and coatings can be sprayed at rates up to 15 lb/hr using a nitrogen-hydrogen plasma. Free standing forms of tungsten are made by depositing a coating of the desired thickness on a shaped mandrel, which is subsequently removed. The tungsten shell may or may not be then heat treated for stress relief or densification. Complex contoured shells have been sintered to close to maximum theoretical density using this method. Thin walled Al_2O_3 radomes up to approximately 16″ in diameter and 42″ in length have been produced experimentally by flame spraying the Al_2O_3 on a shaped mandrel to the desired wall thickness, removing the mandrel, and then sintering to close to maximum theoretical density. The normally high shrinkage on sintering a cold pressed shape was considerably reduced and warpage and cracking were almost entirely eliminated.

Practically all flame spray work is done in air atmosphere, and therefore, the effects of oxygen and nitrogen on the material being sprayed must be considered. The plasma flame technique is the only one adaptable for use in completely controlled atmosphere spraying, and considerable laboratory work is now being done. Unless a powder feeder can be completely isolated from air atmosphere, all components in the spray system must be enclosed within a sealed chamber, which is evacuated and then filled with the desired gas. This is the only method by which the effect of oxygen and/or nitrogen on the substrate and the sprayed material can be entirely eliminated. It permits heating the substrate to any temperature desired, the spraying of any material without atmospheric contamination, and deposition of coatings at the higher temperatures which promote maximum coating density.

Throughout the entire previous discussion, reference was made to materials sprayed using the various spray techniques only as regards their general classification as metals or ceramics and their melting points, without regard to other properties which radically affect the sprayability of each individual material and the quality of the deposited coatings. This was done in order to more simply classify those materials which could be sprayed using each of the known flame spray techniques. Actually, all of the properties of a given material are important in determining sprayability. Besides melting point, thermal conductivity, emissivity, specific heat, transparency to radiation, latent heat of fusion, boiling point, latent heat of vaporization, resistance to oxidation and/or to chemical combination with an element or elements in the heating medium, and the state of any oxides which do form are all important in determining, for instance, the particle size range of a powder to be sprayed and, to some extent, the type of powder spray equipment that can be used. Metals must be capable of being formed into wire in order to be useful with the wire spray technique. Ceramics must be capable of sintering into straight lengths of rods of consistent diameter without binder materials at reasonable temperatures if high purity materials are to be sprayed using the rod spraying technique.

New materials must be thoroughly investigated prior to experimental flame spraying. Toxic materials such as lead, cadmium, beryllium, and possibly boron, (to name only a few) and their compounds or alloys are an ever present danger, not only to the flame spray operator, but to all other people in the immediate vicinity. Special precautions to guard against poisoning must be taken unless a material is known to have no toxic effect. Fortunately, with most materials, the normal exhaust systems recommended for flame spray work are sufficient to protect an operator and the area around him. Pyrophoric materials in powder form—titanium and zircomium for instance—can only be handled and sprayed under complete atmosphere control.

Each one of the flame spray techniques in common use today appears to have its own field of particular usefulness, and no one appears capable of completely replacing another. Wire spray equipment is capable of spraying practically any material which can be formed into wire and, in addition, will spray almost any ceramic with a melting point less than around 5000°F. in rod form. The conventional air-feed powder spray equipment will spray most metal powders including the self-fluxing hard-facing materials, and is particularly useful in spraying those materials with melting points less than around 3000°F. Airless powder spray equipment is most useful in spraying the self-fluxing alloys and practically any other metal or ceramic with a melting point up to about 5000°F. Practically any material in powder form, up to and including some carbides which melt at over 7000°F. can be sprayed using the plasma flame technique. It is most useful, however, for spraying the higher melting point refractory materials and materials such as copper and aluminum where ultra high density and purity are required.

Research of new materials, spray techniques, and equipment offers promise of major improvements in the kind and quality of flame sprayed coatings within the next few years. There is hope of extending their range of usefulness into the higher temperature ranges in use in industry, and improving corrosion and oxidation resistance of the materials themselves and the substrate structures on which they are deposited.

THE ELIMINATION OF EXPANSION BELLOWS AND SPIRALS BY USE OF COMPRESSION STRAIN

H. A. KAMPHAUSEN
University of Melbourne, Parkville
Victoria, Australia
Read by
W. E. BARR
Gulf Research and Development Co.
Pittsburgh, Pa.

I am very happy to be given the opportunity to have this paper read at a Symposium of experts, who will be able to judge the potential use of its content and I will be very pleased to have their comments.

Having followed the rapid growth of the A.S.G.S. from a distance, I envy members the opportunities provided by this organization and the associated American industries; however, I can join you in spirit.

As the title indicates, this paper is concerned with one successful attempt in a field which I consider has been either very much neglected or else has been thought not worth pursuing—I refer to the question of "compression strain and its consequent use in the field of glass-instrumental technique".

At the turn of the century, Otto Schott employed to advantage "compression strain" with his Verbund or "Robax" glass, (manufacturing has been discontinued) although even today the potential use of this strain may not be fully appreciated.

As you know, the motor-car industry is quite concerned with the application of compression strain in considerations relating to car-windows, and this has proved a happy ground for controversy among those who may prefer *cement* laminated windows and those who prefer to use compression strain in a homogeneous glass-window.

The principle involved in a *sealed* laminated glass tubing is that we have two layers of glass—one layer having sealed on its inside a thin layer of glass of lower expansion, so that the tube overall is after cooling in a state of compressional strain. Fig. 1. There is, of course, a danger of introducing a tension along the length of the tubing. To overcome this danger—only a very limited difference in expansion (approximately 5%) *is* permissible.

The application of this principle will now be considered.

Compression strain is sometimes used in the manufacture of glass-metal seals either purposely, for instance in the tempering of a hot pressed button by jets of cold air in the process of Electronic Valve Making, or fortuitously as it is used when tungsten (expansion coefficient α 43.6×10^{-7}) is sealed into silica tubing (expansion coefficient α 5×10^{-7}), by the use of one or two glasses of intermediate expansion. Then effects of the difference in expansion are avoided by the introduction of the maximum stress in the axial direction as a compression strain, and the consequent high radial tension, thus introduced, does not cause a freeing of the

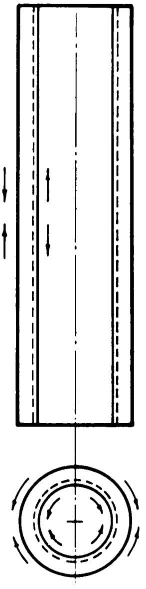


Figure 1

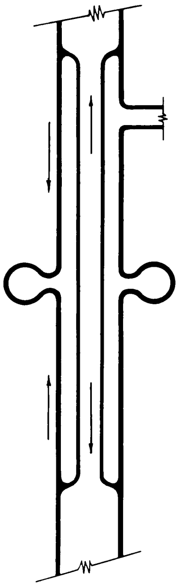


Figure 2

metal from the glass if the seal is made properly without the formation of a layer of tungsten oxide.

We will now consider the theme of this paper.

The construction of expansion bellows is frequently discussed in textbooks and papers. The use of such bellows arises when glass tubes, sealed together at both ends, (one inside the other) are exposed to high temperature differences—for example in distillation columns—and the construction of such expansion bellows, without a lathe, can be a very difficult undertaking.

However, by using two glasses of different expansion, one can partly overcome the effects of temperature differences—the strength of the seals being considerably enhanced by the concurrent introduction of compression strain. Under normal circumstances, the inner tube is exposed to the higher temperature while the jacket remains at room temperature, and an empirical calculation indicates that the difference in expansion coefficient between the inner and outer tubes would be approximately $\alpha .32 \times 10^{-7}$ to $\alpha .40 \times 10^{-7}$. If the difference is much higher, the stress which arises longitudinally would need compensation, whether or not the apparatus is in use. Fig. 2.

Before commencing this investigation, I found, in searching the literature, that the prospects for sealing two glasses for the desired effect were not encouraging.

A. Krings, in a lecture to the "Deutsche Glastechn. Gesellschaft" 13th April 1961, stated that very few papers related to the sealing of different glasses have been written, and his only relevant reference was the statement of C. D. Redson (*J. Soc. Glass Technol.* **39** 1955 P.N3—

10) in connection with radio valves—that "the bulb must be of a optimum expansion to match the stem". Also D. H. Lober ("Glashutten Handbuch" T 3—2 Verarbeitung vor der Lampe) stated that "if one glass should be sealed into another, the maximal allowable difference in expansion must be only 5%". [But we have found that Dr. Lober's statement is only valid in the case of glasses under tension, i.e. when the jacket has the lower expansion.]

Although these reports were not encouraging, we continued our experiments and found that we could obtain a strong seal from English borosilicate glass ($\alpha.32 \times 10^{-7}$ sealed inside Australian borosilicate glass (approx. $\alpha.40 \times 10^{-7}$). In contrast, seals of English borosilicate, inside G-20 ($\alpha.47 \times 10^{-7}$), only remained intact at one end—obviously indicating that the difference in expansion between English borosilicate and G-20 is too great to be used freely to obtain seals at both ends. Figure 2.

The highlight of our experiments was the moderately successful sealing of silica tubing into English borosilicate. Four silica tubes, approximately 12 mm. in diameter, were sealed into borosilicate tubing 25 mm.,—the only difference between them being in the shape of the sealing funnel employed. They were not heat-treated 'i.e. annealed". Two tubes, Fig. 3, cracked after 22 days and 24 days compared with the other tubes, Fig. 4, which lasted only 15 and 16 days. However, silica tubing sealed inside borosilicate glass according to Fig. 3, and subsequently annealed, cracked only after 16 months. In further work, we employed only the seal of Fig. 3. The interesting feature is, that the seal itself never cracked, but the enormous compression apparently caused tension at (A) (Fig. 5) of magnitude sufficient to shear the tubes cleanly, as though cut by a knife.

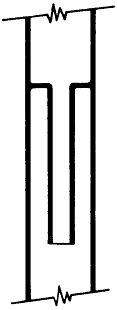


Figure 4

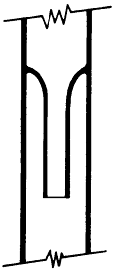


Figure 3

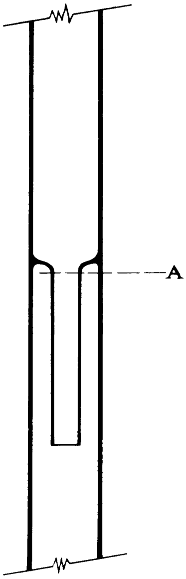


Figure 5

Encouraged by these results, we constructed a Liebig condenser, with the internal tube of English borosilicate glass 18 mm. diameter, the jacket of Australian borosilicate glass 35 mm. diameter, 40 cm. long, with no annealing being carried out. This condenser was then tested with the following liquids, refluxing at asmospheric pressure.

Liquids	*Temp.*	*Time (Hrs.)*
Xylene	140°	6
Cyclohexanol	161°	4
Dichlorobenzene	179°	4
Acetophenone	200°	4
Nitrobenzene	210°	½

During these tests, the water jacket was emptied and later refilled; no failure in the seals occurred.

The condenser, as constructed, also passed the following tests satisfactorily:

(i) The inner tube was filled with liquid air (–170°C.) and boiling water immediately poured over the jacket.

(ii) The inner tube was cooled to –170°C., and then boiling water was poured down it.

Another condenser, with inner tube 16.5 mm. diameter and outer jacket 1.40 m. long and diameter 40 mm., was similarly tested and proved adequate in all respects.

A fractionating column of dimensions similar to those used in the second condenser, but with an evacuated jacket, was successfully used for liquids with boiling point up to 210°C. Liquids with higher boiling points than this were not tried. In all these constructions annealing was omitted.

Rather than making complicated calculations of strength—allow me to quote two small paragraphs out of an article by Charles De Woody—"Fusion" Vol. VI November 1959 P. 25 —31.

"EXPANSION BELLOWS"

"Glass has no region of plasticity between elastic limit and fracture, where deformation takes place continuously. Hookes law holds up to the breaking point, that is to say, the ratio of the applied stress (F/A) to the deformation (strain/unit length) is a constant. In actual practice, however, extraneous factors outweigh theoretical considerations in 'guestimating' the strength of glass."

"Simply to show how absurd we can get, we can quote a few figures 'The maximum strength of glass calculated from molecular cohesive forces would be about 3 million lb./in.^{2}. The maximum strength of borosilicate glass, determined experimentally, is so much smaller than the theoretical value that it is necessary to account for this discrepancy. Considerable amount of work has been done in attempts to establish both the nature and magnitude of cohesive loss. Unaccountable inaccuracies of as much as ± 30% were encountered in carefully controlled experiments so that the strengths previously mentioned could be 13,000 or 7,000 lb./in.^{2}."

To satisfy the skeptic, I would like to add that several hundred sealed-in condensers, and other equipment used for teaching purposes, have been constructed upon the principle employed here—using glasses of different expansion. Prior to this innovation, there was a very high breakage rate observed but this has now been reduced to a very low level.

ACKNOWLEDGMENT

The author wishes to acknowledge the "courage" and assistance of Mr. D. G. Howthorne and Mr. L. G. Sparrow during the experimental test carried out.

REVIEW OF THE SOLDER GLASS SITUATION

K. G. LUSHER
Consumer and Technical Products Division
Owens-Illinois Glass Company
Toledo, Ohio

Solder glass is the name given to a glass which has a lower melting point than the more common glasses such as soda-lime or borosilicate, thus enabling its use as a sealing or bonding agent for other higher melting materials, including glasses, ceramics and metals.

Two basic types of solder glasses are available, vitreous, and the devitrifying types. Each has certain properties and characteristics which distinguishes it from the other. A vitreous solder glass is simply a low melting glass which can be remelted repeatedly. The solder glass can be applied by a cold paste method by mixing the powder with a vehicle, or it can be melted in a platinum crucible to a temperature above its melting point when its viscosity approaches that of water, and parts can be dipped into it.

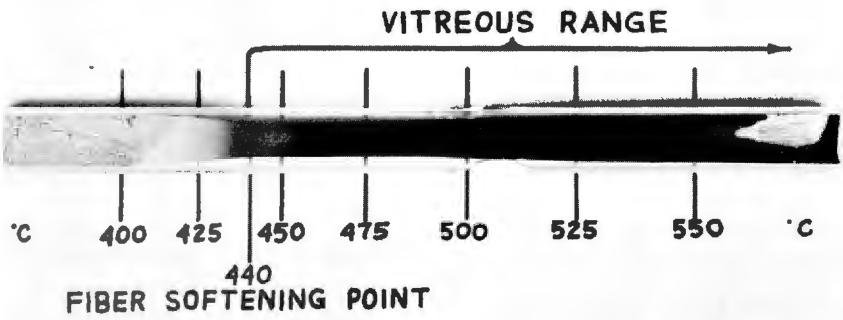


Figure 1

Kimble SG-67 Vitreous Solder Glass (Boat Test)

A gradient boat test made on a typical vitreous solder glass shows the transformation from the powder to the glassy phase. The temperature at which this occurs is near the fiber softening point. Figure 1 shows SG-67 solder glass and this point is at 440° Centigrade.

Devitrifying solder glasses differ from vitreous types in that crystals grow within the glass during curing, forming a crystalline product which is applied by cold application methods only. In gradient boat tests these solder glasses pass through a glassy phase similar to the vitreous types, and then proceed to devitrify upon further heat treatment. Figure 2 shows the CV-101 solder glass, where the fiber softening point is at 373° Centigrade.

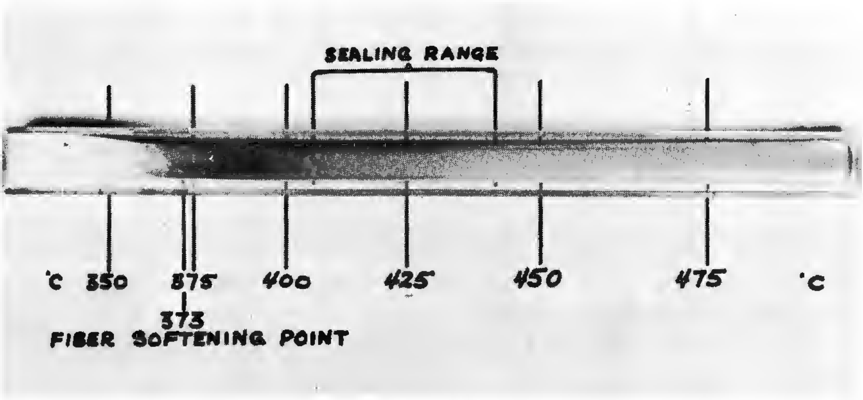


Figure 2
Kimble CV-101 Devitrifying Solder Glass (Boat Test)

Figure 3
Photograph Showing Crystal Growth

The sealing range is 405° to 440° Centigrade for one hour.

During devitrification, crystals grow from small nucleii scattered throughout the solder glass in a random pattern. (Figure 3.) Both time and temperature affect the rate of crystal growth. (Figure 4). In CV-130 solder glass, the rate of crystal growth with temperature can be compared. From the chart it can be seen that the rate of crystal growth at 470° Centigrade is about twice that at 450° Centrigrade, for identical curing times.

Time has also been found to influence devitrification. (Figure 5.) The glassy range decreases and the devitrification range increases as the curing time is increased.

When devitrification starts, the volume of crystalline phase to glassy phase is small. As it continues, more of the total volume becomes crystalline at the expense of the glassy phase, so that at the completion of the curing cycle, the majority of the solder glass is crystalline, being bound together with thin glassy matrices.

Consideration should be given to both the use and the properties desired in the selection of the proper type solder glass. In the accompanying table (Figure 6), some of the more dominant characteristics of both the vitreous and devitrifying types are compared.

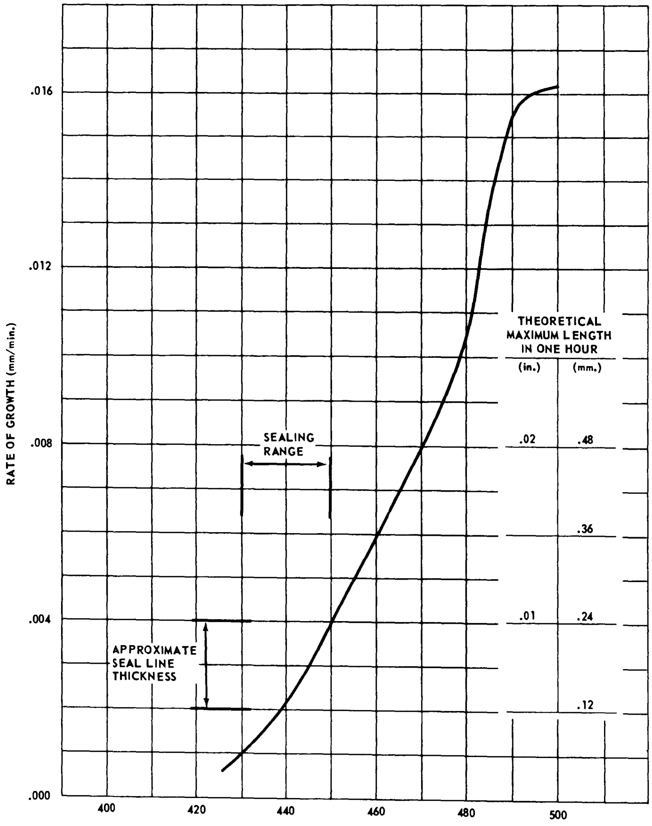


Figure 4
Rate of Crystal Growth VS. Temperature—CV-130 Devit. S.G.

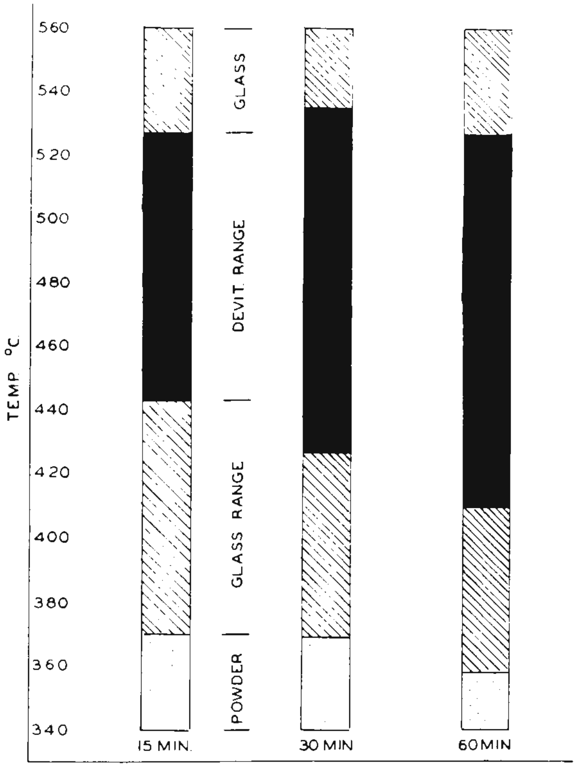


Figure 5
56-130 Solder Glass—Time in Devitrification Furnace

	VITREOUS SOLDER GLASS		DEVITRIFYING SOLDER GLASS
METHOD OF APPLICATION	HOT DIP	COLD PASTE	COLD PASTE
CURING CYCLE	SHORT	LONG	LONG
SEAL STRENGTH	HIGHER	LOWER	HIGHER
ELECTRICAL RESISTIVITY	HIGHER		LOWER
DIELECTRIC CONSTANT	LOWER		HIGHER
SEPARATION OF SEALED PARTS	PARTS EASILY SEPARATED BY REMELTING		PARTS SEPARATED BY CHEMICAL REMOVAL OF SOLDER GLASS

Figure 6
Comparison of Vitreous and Devitrifying Solder Glasses

In some applications in which only one property, such as thermal expansion, might be a factor, either a vitreous or a devitrifying type may be used with equal effectiveness.

Solder glasses are available in a range of thermal expansions in both the vitreous and devitrifying types. (Figure 7). The accompanying table (Figure 7), shows some of the solder glasses with their properties offered by Owens-Illinois Glass Company.

It is necessary that the solder glass match the thermal expansion of the base material to which it is applied. Mismatches of five to ten expansion points can be tolerated in some cases, but these limits should not be exceeded. Any mismatch will cause stresses to be developed in both the solder glass and the base material which could cause failures in cooling or during use of the assembly. It has been found in practice that slightly more mismatch can be tolerated when the solder glass layer is kept thin, than if it is thicker. Figure 8 shows expansion curves for some solder glasses compared with some of the common glasses.

The expansion of devitrifying solder glasses is influenced by the time it is held at a given temperature. A longer curing time at a certain tem-

Solder Glass Number	*Type*	*Cur. Temp. for 1 Hr.*	*Thermal Expansion x 10^{-7}/°C.*	*Seals to: (Materials)*
SG-7	Vitreous	590°C[1]	46 (0-300°C)	Kovar metal. EN-1, K-650, N-51-A glasses.
SG-67	"	430°C[1]	82 (0-300°C)	TM-5, KG-12, KG-1, R-6 glasses.
SG-68	"	430°C[1]	90 (0-300°C)	TL-2, TM-3, TH-10
CV-97	Devit.	440°C	93.5 (0-300°C)	Sylvania No. 4 alloy metal TM-5, KG-12, KG-1, R-6 glasses.
CV-101	"	425°C	92 (0-300°C)	Sylvania No. 4 alloy metal TM-5, KG-12 glasses.
CV-130	"	425°C	107 (0-300°C)	No. 430 alloy metal TL-2, TM-3, TH-10 glasses.
CV-137	"	435°C	97 (0-300°C)	Sylvania No. 4 alloy metal TM-5, KG-12, KG-1, R-6 glasses.
CV-285	"	625°C	55 (0-300°C)	Alumina and beryllia ceramics.
CV-635	"	685°C	36 (0-300°C)	EE-2 glass.
CC-10	*	425°C	101 (0-300°C)	TL-2, TM-3, TH-10 glasses.

[1] Underload

*Devit.—Electrically Conductive

Figure 7
Solder Glass Information Data

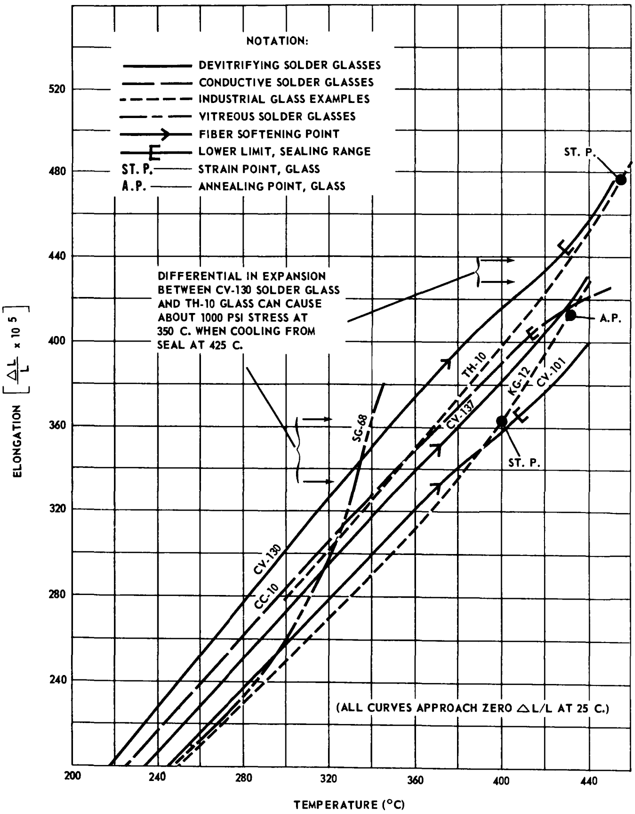


Figure 8
Thermal Expansion of Solder Glasses

perature usually produces a lower expansion than a shorter cycle at the same temperature. This change in expansion shows up as stress developed in the material to which the solder glass is sealed. Figure 9 demonstrates what happens to CC-10 conductive solder glass cured at time cycles of fifteen minutes, thirty minutes, forty-five minutes and sixty minutes. The desirable working range in this instance is actually in an area where the base glass was in compression. For CC-10 solder glass, firing for short periods such as for fifteen minutes, or at low temperatures such as 400° Centrigrade, produces seals of questionable vacuum tightness. Firing for longer periods, such as sixty minutes or more, or at temperatures of 450° Centrigrade or above, produces a product having decreased electrical conductivity. Figure 10 shows a boat test made on CC-10 solder glass with the conductive range indicated.

The standard vehicle usually supplied for solder glass applications is a mixture of $1\frac{1}{2}\%$ nitrocellulose in amyl acetate. This is mixed with the solder glass powder to form a paste which can then be applied by spatula or extrusion method to the part. Drying can be done in room air in approx-

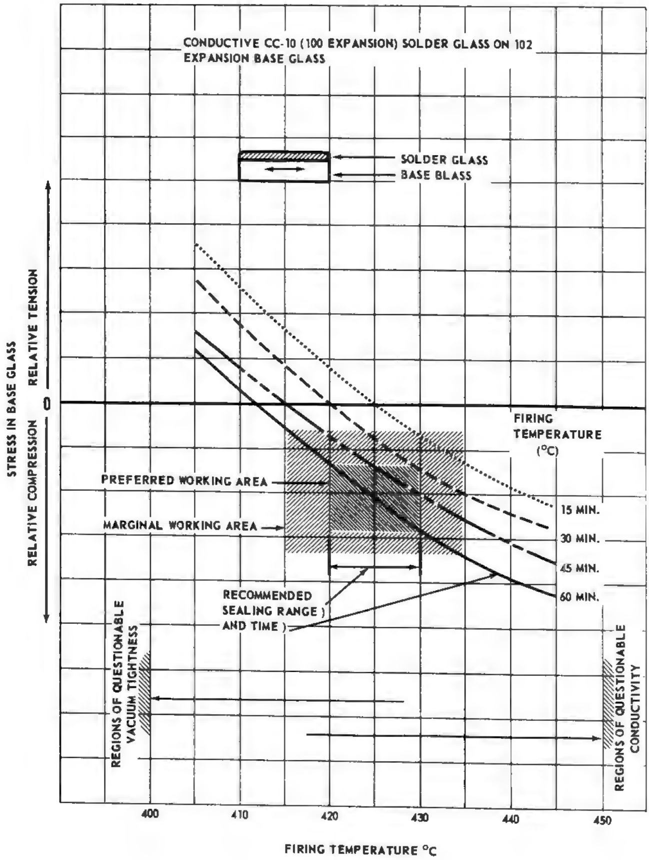


Figure 9
Seal Stress VS. Firing Temperature and Time

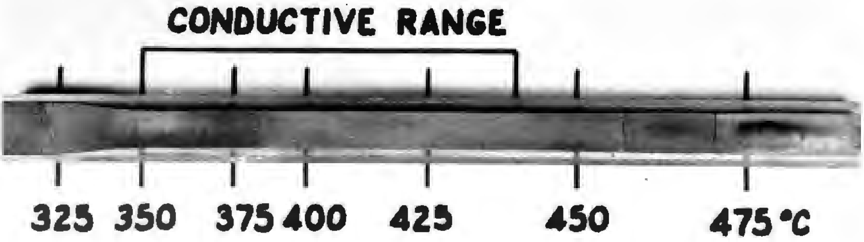


Figure 10
Kimble CC-10 Conductive Solder Glass (Boat Test)

imately fifteen minutes, or the time can be decreased through infra red heating. This produces a product which has sufficient green strength and adhesion to the part to allow moderate handling and storage. One serious disadvantage of this vehicle is its high rate of evaporation. Good ventilation should be provided in the area in which it is used for health reasons. Because of the rapid evaporation rate, the paste must be applied almost immediately after mixing, limiting the methods of application to a spatula or extrusion from a tube. In many instances, other application methods such as by cold dipping, doctor blade, brush, roller coating, spraying, or by silk screen, may be preferred.

Vehicle	*Drying Rate*	*Residue After Curing*	*Recommended Application Method*
1½% nitrocellulose in amyl acetate	Fast	No	Spatula, extrusion, spray
8% butyl methacrylate in butyl carbitol	Slow	No	Spatula, brush, roller coat, cold dip, doctor blade
Vitrol oil 30B	Very Slow	Yes	Silk screen, cold dipping
Harshaw P-529 oil	Very Slow	No	Silk screen, cold dipping
Mixture: (by weight) 47.9% distilled water 47.9% isopropyl alcohol 0.2% 10% magnesium sulphate solution 4.0% ethylene glycol	Slow	No	Spray, roller coat, brush, doctor blade, cold dip, spatula

Figure 11
Solder Glass Vehicle Study

Several other vehicles were studied in an attempt to reduce the evaporation rate. Figure 11 shows five vehicles which were studied, indicating the drying rates, the residues left after curing, and the recommended application methods for solder glass mixtures made using these vehicles.

SUMMARY

Although solder glasses were originally developed to serve as a sealing material for glasses, ceramics and metals and combinations thereof, other uses are continuously being discovered. Mixtures of solder glass with metal, glass or ceramic powders can be made which have unique properties. It has been found that when silver, iron, tin, zinc or graphite powder is added to solder glass, electrically conductive products of varying resistivities result. Resistivity of a mixture is controlled by the amount of metal powder added. The addition of iron produces a solder glass with magnetic properties for instance.

In addition to being used in paste and paint forms, vitreous type solder glasses can be melted and formed into shapes by pressing, drawing, or blowing, using standard glass working techniques. Composites and preforms can be made, employing powder metallurgy techniques, using solder glass as the material or in a mixture with other materials. In the electronics industry, solder glasses are being tried in critical encapsulation and sealing applications.

Solder glass is a new material having certain behavior characteristics and use limitations. Like all other new materials, its future will depend largely upon the imagination of those who use it.

REFERENCES

1. "Technical Data, Kimble Glasses." Published manual, Owens-Illinois Glass Company, Toledo, Ohio. (1963-1964).
2. United States Patent 2,889,952, to Claypoole, June 9, 1959.

SEALING OF GLASS TO SINGLE CRYSTAL AND POLYCRYSTALLINE MATERIALS

FRANCIS W. MARTIN
Technical Staffs Division
Corning Glass Works
Corning, New York

I. INTRODUCTION

A number of factors must be considered when undertaking the sealing of single crystal materials to glass.

Since both are rigid materials it is essential that the expansion be matched over the interval between room temperature and the temperature where the glass becomes rigid (setting-up point). The crystalline material should preferably be isotropic in its expansion and should have no phase transformations in the temperature interval where it is effectively joined to glass.

In making the seal one must maintain a reasonably low temperature gradient in the crystal so as to avoid thermal breakage. Glasses yield viscously at temperatures above their strain point and so are subject to heat shock breakage only at lower temperatures. Crystalline materials, on the other hand, are subject to heat shock breakage at all temperatures.

The most common form of seal involving a single crystal material is that of a flat disc or window in a glass apparatus. The glass apparatus may be made of a suitably matching glass or else the window may be sealed to an equal diameter graded seal, the other end of which is joined to the apparatus glass; for example, Corning's Code 7740 glass.

Even where the window is joined to an extensive apparatus of matching glass, evacuation usually requires a graded seal to Code 7740.

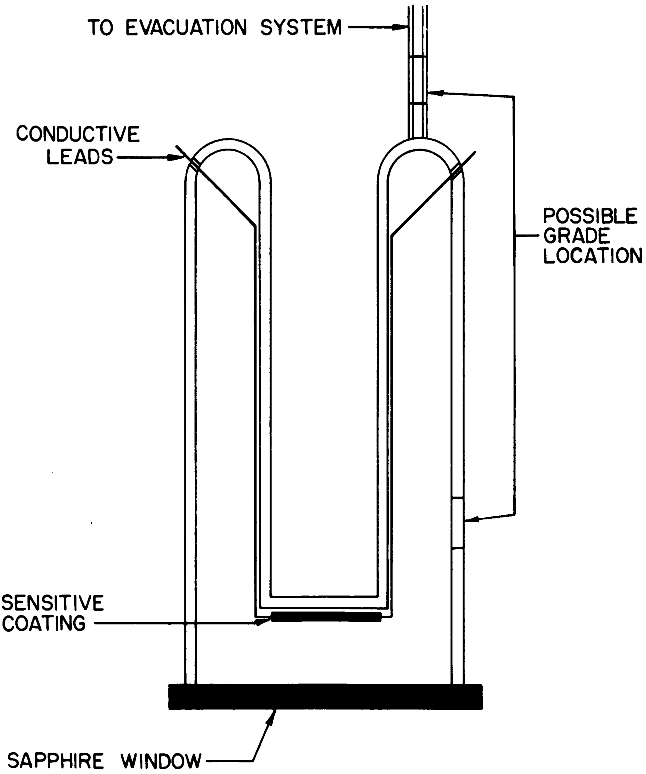
Likewise the introduction of conducting leads requires grades to glasses appropriate for lead sealing such as Codes 7720 or 3320 for tungsten, and Codes 7052 or 7056 for Kovar or molybdenum.

In making a seal to a single crystal material there are two basic methods. The single crystal material can be sealed to glass directly or sealed through a thin layer of a much softer glass (solder glass method).

II. SEALING SINGLE CRYSTAL SAPPHIRE TO GLASS

Interest in the use of synthetic single crystal sapphire (alumina) for windows stems largely from its infrared transmitting properties. There are, however, some applications where the excellent heat conductivity is the feature sought. The window usually is in the form of a flat disc although dome-shaped structures are also used.

Infrared cells generally resemble a thermos bottle in construction. The infrared sensitive film is deposited on the inner member opposite to the window. The inner tube is refrigerated by means of a liquid medium or a metallic cold finger (see Fig. 1). In some cases the sensitive layer is deposited on a second sapphire window sealed to the end of the inner arm. The excellent heat conductivity of sapphire at low temperature aids in maintaining the sensing surface at a uniform low temperature.



TYPICAL I-R CELL STRUCTURE

Figure I

Of quite different geometry is an apparatus described by Nelson and Spindler[1]. Here a cylindrical tube is ground out of a large boule of sapphire. The problem was to join both ends to glass tubing so that electrical leads could be introduced and a surrounding glass envelope joined thereto. The apparatus was used in flash photolysis studies.

A. Expansion Match

For joining sapphire to glass a good expansion match is quite essential. Alumina has an elastic modulus much higher than glass; therefore, the stress in the glass will be higher for a given mismatch than in a glass-glass seal. Usually there is a certain amount of expansion anistropy in the plane of the disc so some compromise is necessary.

The expansion curve for sapphire has a minimum value for directions perpendicular to the optic axis. The maximum expansion is in the direction of the optic axis.

The expansion in any direction making an angle θ to the optic axis is:

$$K = K_A + (K_B - K_A)\cos^2\theta \qquad (1)$$

where K_A is the expansion perpendicular to the optic axis
K_B is the expansion parallel to the optic axis.

For any disc whose plane is not perpendicular to the optic axis, there will be one direction in the plane of the disc which is perpendicular to the optic axis. In this direction the expansion will be a minimum (K_A). At right angles to this direction the expansion will be a maximum. The expansion can be as high as K_B. For the special case of a disc cut perpendicular to the optic axis the expansion is K_A in all directions. This is the most desirable situation.

In the hydrothermal method of growing crystals the growth axis (long dimension of boule) is about 37° from the optic axis.

A straight cut across the boule would produce a disc with maximum and minimum expansion as follows:

$$\begin{aligned} K_{min} &= K_A \qquad (2)\\ K_{max} &= K_A + (K_B - K_A)\cos^2 53^\circ\\ &= .637\,K_A + .363\,K_B \end{aligned}$$

Where discs are cut parallel to the cleavage of a split boule the situation is less favorable

$$\begin{aligned} K_{min} &= K_A \qquad (3)\\ K_{max} &= K_A + (K_B - K_A)\cos^2 37^\circ\\ &= .363\,K_A + .637\,K_B \end{aligned}$$

Finally, it might be noted that the average expansion of sapphire (one-third the volume expansion) is:

$$K = \tfrac{2}{3}K_A + \tfrac{1}{3}K_B \qquad (4)$$

This is the theoretical expansion for a 100% polycrystalline body. Actual alumina bodies might be slightly different due to other crystalline phases, solid solution and residual glassy phases.

In Fig. 2 the maximum and minimum expansions (K_A, K_B) of single crystal alumina are given for the temperature range 350°-650°C. The curves all meet at room temperature which is out of the figure. Polycrystalline alumina plots as a single curve very near to the theortical position (one-third of the interval from the bottom curve).

The glass which has proved to be most suitable for direct sealing of sapphire is Code 7520. Its expansion curve is also given in Fig. 2. The annealing and strain points are indicated.

Some people have had success in sealing small windows with Code 7052. The mismatch is quite large but in a favorable direction since the hoop stress in the glass is compressive. The tensile bending stress at the outer surface of the glass may be masked somewhat by compressive stresses resulting from a rapid cooling of the seal.

As indicated in Fig. 2, Code 7280 is a fairly good match to sapphire.

When sealing is accomplished by means of a softer glass (Code 1826) the set point is at a lower temperature and Code 7280 shows a more favor-

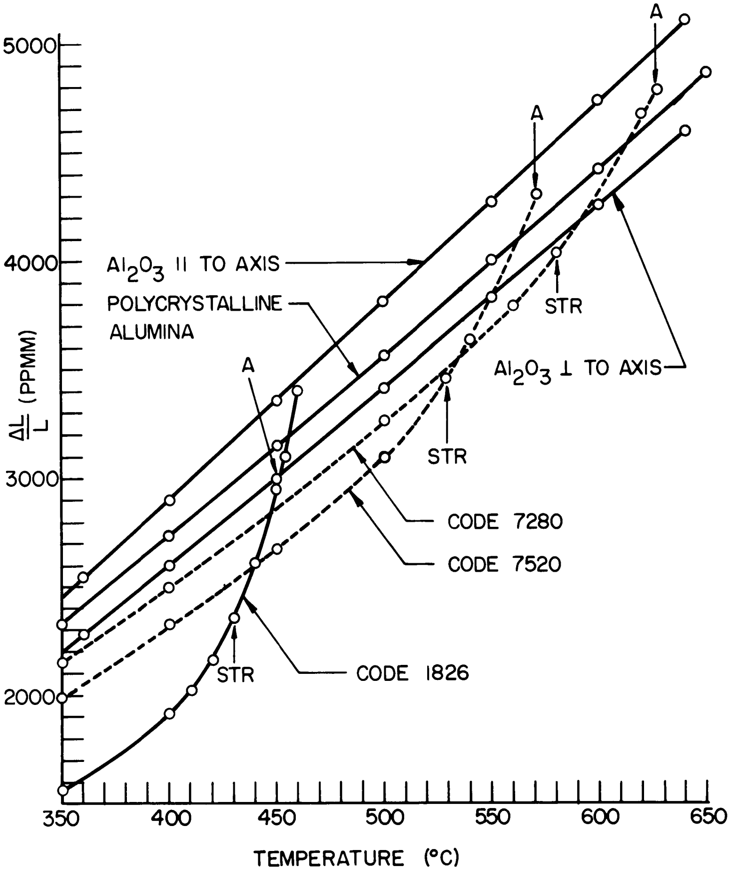


Figure 2

able match than Code 7520. The expansion curve for Code 1826 is also given in Fig. 2.

B. GRADED SEALS TO CODE 7740 GLASS

As noted above, there is usually a requirement for grading to Code 7740 glass if only for evacuation purposes. In addition, it is sometimes necessary to grade to a glass appropriate for introducing Kovar, molybdenum or tungsten leads.

There are several methods of grading to Code 7740 glass. Since Code 7520 is glass #3 in a standard graded seal package sold by Corning Glass Works, it can be joined by the two intermediate glasses (#1 and #2).

For larger diameter seals it might be desirable to use more grade steps. A useful sequence is:

Code 7520, Code 7052, Code 7050 or Code 7750, Code 7070, Code 7740.

Another sequence that involves harder glasses and which is particularly desirable in grading from Code 7280 is:

Code 7280 or 7520, Code 7800, Code 3320, Code 7740.

Kovar sealing glasses can be sealed directly to Code 7520. Molybdenum can also be sealed through Kovar sealing glasses. For tungsten seals, Code 7750 can be joined via Code 7052. Code 3320 can also be used via Code 7800.

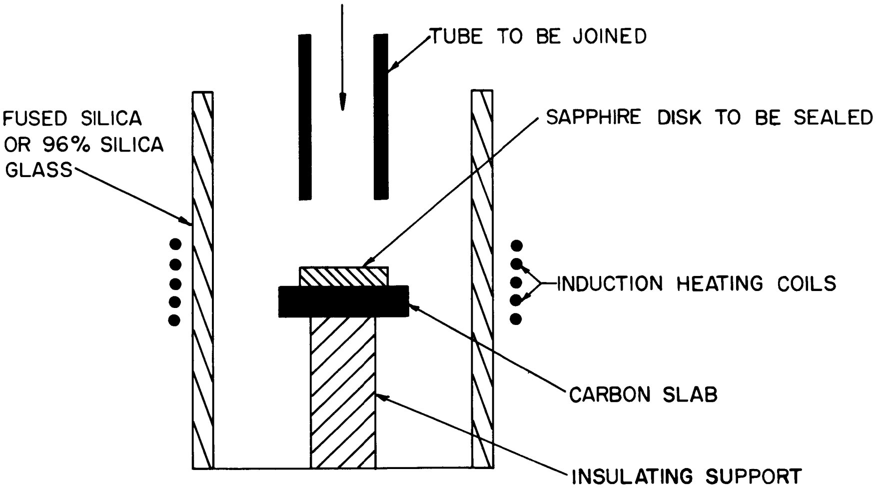
C. Techniques for Sealing

1. *Direct Sealing*

Several methods have been described for the direct sealing of sapphire windows to glass.[2] There are undoubtedly other methods and variations that have been used.

The key feature in all methods is to heat uniformly through the face of the disc. This can be done by placing the disc on a carbon susceptor which is heated by induction.

The hot carbon stage is usually protected from drafts by a surrounding tube which might be made of fused quartz or 96% silica glass. The tubing to be joined is lowered from above onto the hot disc. The end of the tubing to be sealed may be preheated by a gas-oxygen flame before lowering to sealing position. A typical setup is illustrated in Fig. 3.

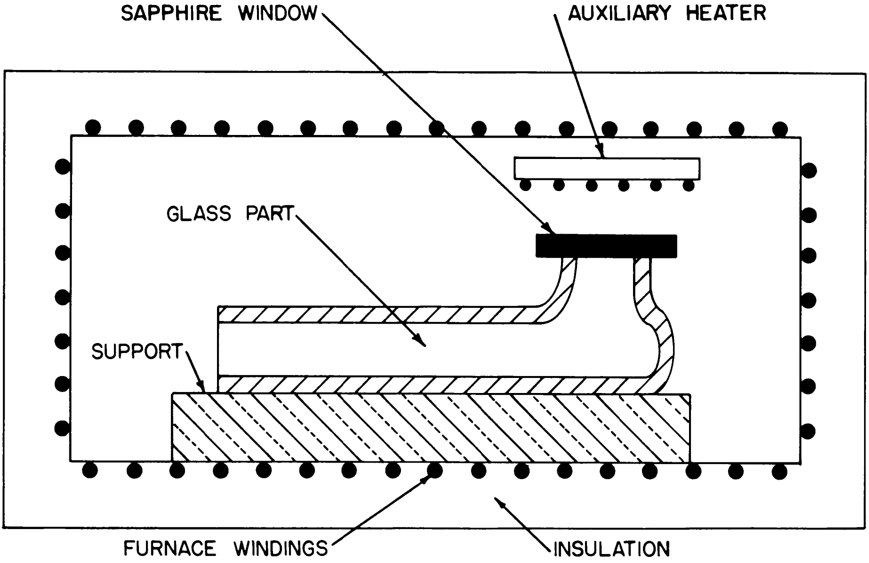


APPARATUS FOR DIRECT SEALING

Figure 3

2. *"Solder Glass" Sealing*

An intermediate layer of softer glass could be used in the method just described but would not provide much advantage. The solder glass method is usually confined to situations where the direct seal is not convenient. Examples are: sealing of large windows and the sealing of windows to short side arms.



FURNACE FOR SOLDER GLASS SEALING

Figure 4

In Fig. 4 one method for sealing a sapphire disc is illustrated. This uses a furnace which has an auxiliary winding that heats the sapphire disc to a higher temperature appropriate for joining. The furnace is maintained at the highest temperature that will not result in distortion of the glass apparatus. The sealing area is given enough additional heat to produce a seal. The annealing range of Code 7280 is high enough to permit sealing in a simple furnace without applying additional heat to the seal area.

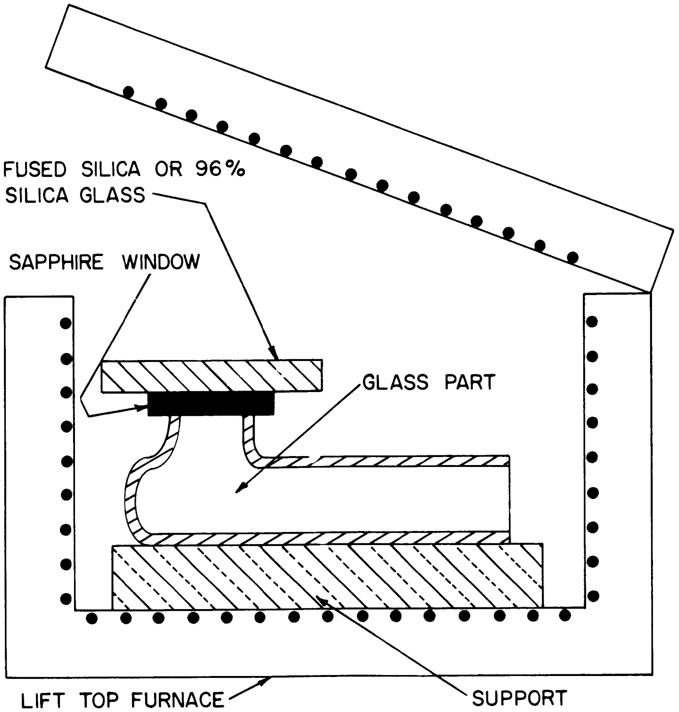
In order to get a good seal to the sapphire it is desirable to preglaze the disc. The Code 1826 can be applied as a slurry of powdered glass in a vehicle such as 1½% nitrocellulose in amyl acetate. After drying, excess powdered glass can be removed where necessary and the disc heated in a furnace. Since there is no temperature limitation in this step, preglazing can be done at temperatures at high as 1000°C.

For sealing, additional solder glass is applied to the glass end of the joint. This is allowed to dry before the glazed disc is put into position.

In some cases it is convenient to apply a little wet slurry around the joined parts to maintain position. The added material should, of course, be allowed to dry before sealing.

In sealing, the furnace is first brought up to temperature, then the auxiliary winding is turned on until the seal is completed. Heating and cooling rates are not critical. However, it is usually desirable to hold the temperature at the annealing point of the envelope glass for a short period during the cooling cycle. The actual temperature at the seal is in the range 650-750°C.

A disadvantage of the above method is that, unless the furnace is equipped with windows, one must work blindly and proceed by trial and error until an appropriate sealing cycle is found. An extra thermocouple to measure temperature in the seal area is very useful.



FURNACE FOR SOLDER GLASS SEALING

Figure 5

A simpler sealing method which has been found to work quite well is illustrated in Fig. 5. Here the parts are assembled in a lift-top furnace with a sheet of fused quartz or Code 7900 glass on top of the sapphire disc. The furnace is heated and held at a temperature above the annealing point of the glass. The furnace top can then be lifted and the seal made by heating through the transparent cover with a gas-oxygen torch. After sealing the lid is closed, the furnace is allowed to equilibriate for an appropriate time and then turned off.

III. OTHER CRYSTALLINE AND POLYCRYSTALLINE MATERIALS

There are other crystalline and polycrystalline materials that can be sealed to glass using the above methods. The first step is to find an appropriate glass. This can best be done by comparing the complete expansion curves. If only average coefficients (0-300°C.) are available, the glass should have an expansion some 15% lower than the crystalline material. In this case it is assumed that the crystalline material is relatively linear in expansion and that the glass expansion is for the linear range below the transformation range.

A. ALUMINA

Polycrystalline materials can be joined to the same glasses noted above for sapphire The usual requirement in this case is to make a glass extension to a ceramic tube.

The usual alumina bodies (85-92% Al_2O_3) can be joined to glass by conventional glass working methods. Higher alumina bodies are quite prone to thermal shock breakage.

Solder glass sealing in a furnace, using Code 1828, is possible but not convenient if the ceramic tube is long. We have been able to seal with Code 1826 in a lathe setup where a surrounding, electrically heated coil is used instead of a flame. This is illustrated in Fig. 6. The coil has a ceramic coating to reduce outward radiation and a hole in the center to allow observation of the joint. Additional solder glass can be applied by a rod through the hole.

B. BERYLLIA

Beryllium oxide has very much the same expansion as alumina so the same glasses and techniques can be used.

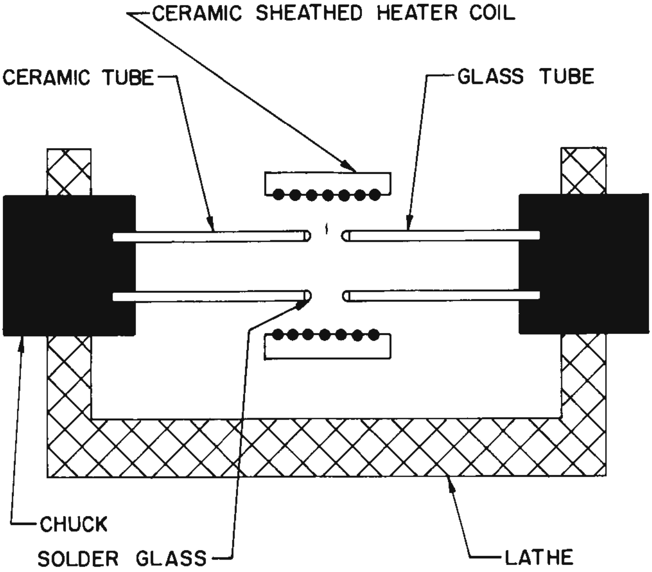
C. MAGNESIA

There is some interest in sealing windows of single crystal MgO (Periclase). The material is cubic and thus isotropic in expansion. A proper glass would be somewhat higher than lime or lead glasses such as Code 0080 or Code 0120 whose thermal expansivities are about $90 \times 10^{-7}/°C$.

Code 0128 glass, which is used in color TV necks, should be an appropriate glass. It can be joined to Code 0120 glass. Solder glass sealing with Pyroceram® brand cement #95 is a good possibility.

D. ELECTRICAL PORCELAIN

Electrical porcelains are fairly low in expansion and have a rather high glassy phase content. It is usually quite easy to join them to a borosilicate glass such as Code 7740 or Code 7720.



CROSS SECTION OF LATHE SEALING ARRANGEMENT FOR SEALING WITH SOLDER GLASS

Figure 6

E. Mullite

Mullite polycrystalline bodies match Code 7720 or Code 3320 quite well in expansion. Small diameter tubes can be joined to Code 7740.

Some mullite bodies have little glassy phase and are, therefore, sensitive to heat shock. Solder glass sealing to Code 1720 with Pyroceram® brand cement #45 is possible. Short sections of Code 3320 or 7720 can also be joined in this way but with some distortion.

F. Silicon

Silicon windows are used to some extent in infrared work. The material is cubic and thus isotropic. From stress observation on seals it appears to be about midway between Code 7720 and Code 7740 glasses and can be sealed to either. No difficulty is encountered in flame sealing. Evidently this material, unlike sapphire, has some ductility.

G. Germanium

Germanium behaves much like silicon but has a higher expansion. A seal using Code 1826 as a solder glass has been reported.[3]

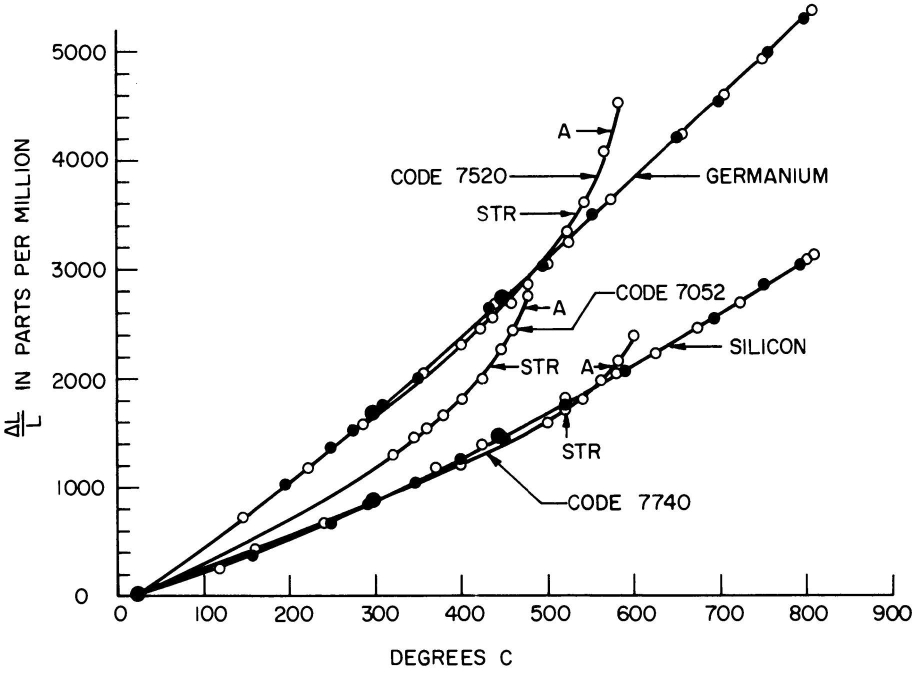


Figure 7

Fig. 7 gives the expansion curve for silicon and germanium together with glasses that might be considered for joining.

REFERENCES

1. L. S. Nelson and G. P. Spindler, *Review of Scientific Instruments,* Vol. 29, No. 4, 324-326, April 1958.
2. Chasmar, Creston, Isaacs and Young, *Journal of Scientific Instruments* **28,** 206 (1951).
   H. Rawson, *Journal of Scientific Instruments,* **28,** 208 (1951).
   M. T. Beardsley and George Greene, "Making and Sealing Synthetic Sapphire Windows to Infra-Red Detecting Cells," *A. F. Technical Report No. 6495,* Sept. 1950.
3. C. R. Snyder, *Fusion,* p. 15, Feb. 1961.

GLASS TECHNOLOGY APPLIED TO INFRARED DETECTOR HOUSINGS

Carl R. Snyder
Special Products Operation
Philco Corporation
Lansdale Tube Division
Lansdale, Pa.

I. INTRODUCTION

Glass, as a structural material for infrared detector housings, has proven itself invaluable to the field of infrared detection. However, the use of glass as the preferred material for housing the detecting elements has introduced new demands on the glassblower and to the field of glass technology. The nature of these demands is seen in a few primary considerations.

Infrared detectors for the most part require a vacuum environment, and to obtain the increased sensitivity available through operation at liquid nitrogen temperatures, a dewar type housing is required.

The detecting element must be able to "see" the infrared rays; consequently, the window material must pass the infrared wavelengths. The window material and the glass housing must be compatible enough to enable a vacuum tight seal between them and should hold up over a wide range in temperature.

Necessary electrical connections to the detecting element must exit through the glass, maintaining high vacuum tight seals.

Loose conductors cause microphonics and cannot be tolerated; therefore, conductors must be an integral rigid part of the housing.

Optical specifications often require tight tolerances on the spacing of the detecting element and the transmitting window. Therefore, special fixturing and sealing techniques are required.

The foregoing considerations indicate the importance of choice of glasses for detector housings, the selection of glass-to-metal combinations, and proper sealing techniques. Only through correct choice of materials and the use of appropriate sealing techniques is it possible to fabricate housings that complement the performance and reliability of the IR detecting elements they contain. The sealing techniques described in this paper are categorized as (1) Window Sealing, (2) Sealing of Electrical Connections, and (3) Precision Sealing.

II. WINDOW SEALING

I shall first describe a sealing technique for synthetic sapphire (Al_2O_3), since it is probably the most widely used window material. This technique is suggested by British sources[1,2] and employs an R.F. induction heating unit.

The glass used is Corning's 7520. Its coefficient of thermal expansion, 60×10^{-7}, closely matches that of sapphire, 65×10^{-7}. The 7520 glass can be sealed directly to 7052, permitting subsequent sealing to Kovar.

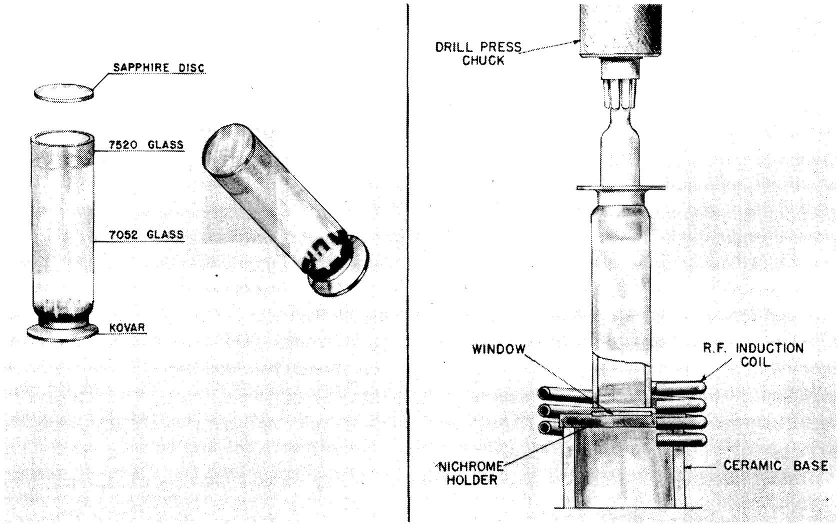


Figure 1

A. Sapphire seal.

B. Sealing setup.

The sealing technique employs a drill press and an R.F. induction heating unit, although more sophisticated fixturing than a drill press can be used, depending on the needs. Figure 1 shows the sapphire-to-glass seal and sealing setup.

The 7520 glass tubing is cut to the desired length. The end to be sealed to the sapphire window is etched in HF and firepolished. The sap-

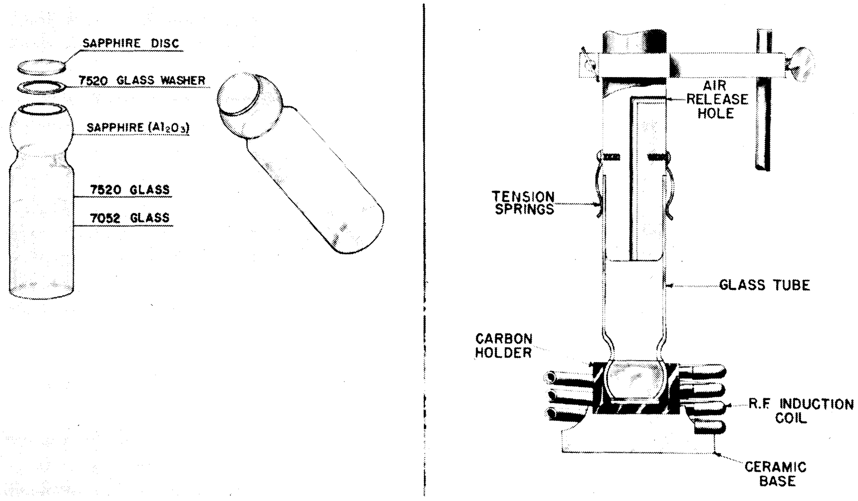


Figure 2

A. Barrel-shaped sapphire seal.

B. Sealing setup.

phire window is rinsed with acetone and placed in a recess of a Nichrome holder (the recess of the holder being no deeper than half the thickness of the window and with approximately 0.005″ clearance on the diameter). The holder rests on top of a ceramic or quartz tube and is placed within the induction coil. The 7520 glass tube is held in an asbestos wrapped holder which is clamped in the chuck of the drill press. The handle of the drill press is turned, lowering the glass tube until it almost touches the sapphire window under the tube. The tube is then lowered so it comes in contact with the sapphire window. The Nichrome holder is heated to approximately 1000°C. Careful observation will note the glass softening and wetting onto the sapphire. At this point the tube is pressed against the window to insure a tight seal. The Nichrome holder is then cooled to just under cherry red. The glass tube with the sapphire window sealed to it is lifted out of the drill press and transferred to an annealing furnace that has been preset to 560°C (annealing temperature of 7520 glass). After a period of no less than 15 minutes the oven is cooled to 300°C over a period of at least 4 hours.

Figure 2 demonstrates the capabilities of sealing sapphire of different geometrics. Because of the difficulty in fabricating sapphire to a full sphere, it was necessary to use a barrel shape and seal off the truncated end with a sapphire disc using a 7520 glass washer between the two. The disc seal and the seal to the main tube are made simultaneously.

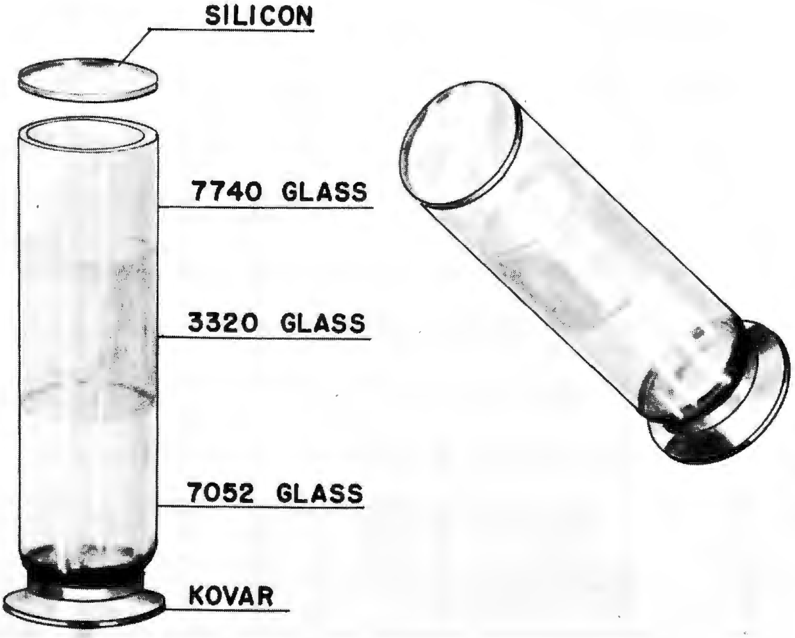


Figure 3
Silicon seal.

Silicon, another infrared transmitting window material, is an excellent match to Corning's 7740 glass. However, since it is necessary to end up with 7052 glass to later effect a seal to Kovar, a standard grade of 7740, 3320, and 7052 is made up as shown in Figure 3 prior to sealing of the window. The sealing procedure and setup is identical to the sapphire sealing technique.

Barium fluoride (BaF_2), a third material with excellent infrared transmission, is desirable as a window material for certain infrared detectors. However, because of its high coefficient of thermal expansion (185×10^{-7}) and its extreme sensitivity to thermal gradients, standard sealing techniques are not practical. A method employed by the author utilizes silver chloride (AgCl) as the sealing medium[3]. The plasticity of AgCl allows for the wide differences in thermal expansion between the BaF_2 and the sealing glass.

As noted in Figure 4, the periphery of the BaF_2 window and the necked-down section of the 7052 glass tube are painted with silver paint. Adhesion of the silver paint is obtained by firing in a furnace at 500°C. A program controller is used to cycle the temperature to prevent cracking of the BaF_2. The furnace is raised (starting from room temperature) to

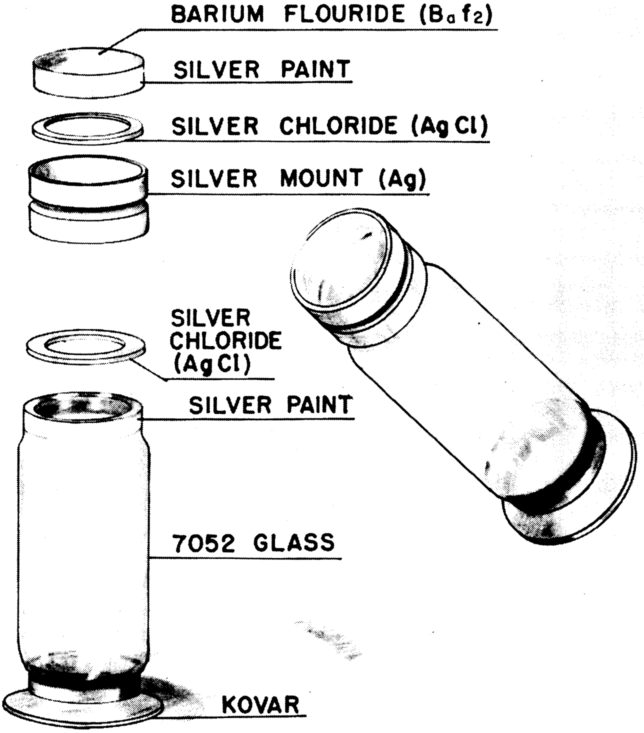


Figure 4
Barium fluoride seal.

500°C over a period of 2 hours and returned to room temperature over a period of 6 hours. The bellows-shaped silver mount is degreased in trichloroethylene, rinsed in alcohol, and abrasive blasted on the inner diameter using an S. S. White industrial air abrasion unit with 50-micron particle size aluminum oxide. This abrasion is used to ensure excellent wetting action of the silver chloride to the silver mount. The components are assembled in the order shown in Figure 4 and placed in a furnace. The furnace is again programmed, with the exception of the temperature limit being 475°C (silver chloride melts at 450°C). The silver chloride wets only the areas painted with silver paint and also the inner diameter of the silver mount. Many mismatched materials may be safely sealed employing this technique.

Figure 5.
Sealing Kovar leadthrus.

III. SEALING OF ELECTRICAL CONNECTIONS

Figure 5 shows the sealing of Kovar leadthrus necessary for electrical connections to the IR detector element within the housing. Small diameter Kovar rods are prebeaded with 7052 glass by Kovar-to-glass sealing techniques. The prebeaded Kovar rods are then sealed through the main body of the housing.

To eliminate lead-generated microphonic noise, lengths of 7052-glassed platinum wire are sealed directly to the inner body of the housing between the Kovar leadthrus and the detector element. Platinum was chosen for this function because of its ductility and its ability to withstand the high temperatures required in sealing to the housing. The platinum wire is limited to 0.010″ diameter to prevent any cracking which might be expected due to the differences in thermal expansion of platinum and that of 7052 glass. A method of glassing the platinum wire is shown in Figure 6. The platinum is first cleaned by immersing it in aqua regia for a few minutes, rinsing in running tap water, and pulling through a cotton swab saturated with alcohol. For ease of handling, the wires are approximately 12″ long. After cleaning, the wires should not be touched with bare fingers. Clean cotton gloves should be worn to prevent contamination from finger grease, which would cause excessive bubbling while sealing. The wires can be straightened one at a time by holding each end with tweezers and passing them through a small hydrogen brush flame. While the wire is heating to a cherry red, a slight amount of tension is applied.

Figure 6
Beading platinum wire.

The platinum wire is threaded through 7052 glass tubing of small diameter. This small tubing is made by heating larger diameter tubing and stretching it. After sealing, the long lengths of glassed wire can be cut into shorter lengths, depending on the distance between the Kovar leadthrus and the IR detecting element.

Sealing the lengths of prebeaded platinum wire to the inner section of the dewar type housing was solved by inserting a heating mandrel, as shown in Figure 7. Power to the heating element is Variac-controlled to permit temperature adjustment. The mandrel is made of Kovar because

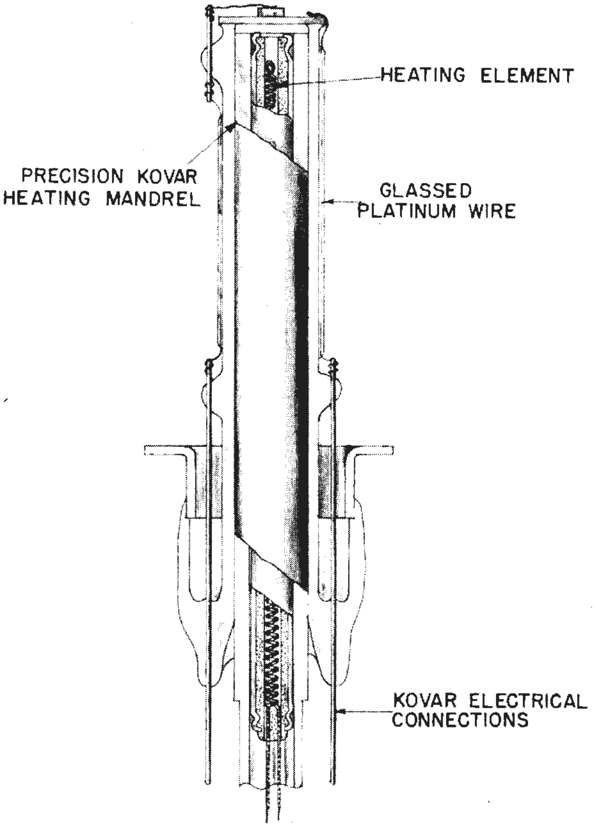


Figure 7.
Cross-section of heating mandrel.

its thermal expansion is close to that of 7052 glass, and is precision machined to a close fit. The mandrel is precoated with a thin Glydag* solution (graphite suspended in glycerine) to prevent fusing of the glass to the Kovar mandrel while sealing the platinum wires to the housing.

After the necessary number of platinum wires are sealed, the housing is slid off the mandrel and placed in a furnace preheated to the annealing temperature of 7052 glass (480°C). Figure 8 shows sealing of the platinum to the housing.

The exposed ends of the platinum wire can be spotwelded and/or soldered to the Kovar leadthrus, after cleaning per Carborundum Co.'s chemical cleaning specification, "file reference 100 EB4."

---

*Glydag is a product of Acheson Colloids Company, Port Huron, Michigan.

Figure 8
Sealing platinum wires to the housing.

Figure 9
Heliarc welding.

IV. PRECISION SEALING

When the IR detector is mounted and processing completed, one of two methods of final sealing of the dewar inner and outer sections is used. Flame sealing was used in the early stages of development but was abandoned because it was found to be a source of contamination to the detecting element and required exceptional skill to maintain the close tolerances required. Housings with Kovar flanges sealed to the ends are heliarc welded with a setup of the type shown in Figure 9. The second method, employing the setup shown in Figure 10, uses R.F. induction heating and makes possible extremely tight tolerances on concentricity and optics.

The inner section of the housing is fixed in a vertical position on a close fitting ceramic (lava) mandrel. A pre-oxidized Kovar washer slightly larger than the O.D. of the housing and with a cross-section slightly exceeding the wall thickness of the glass is placed on the sealing edge of the

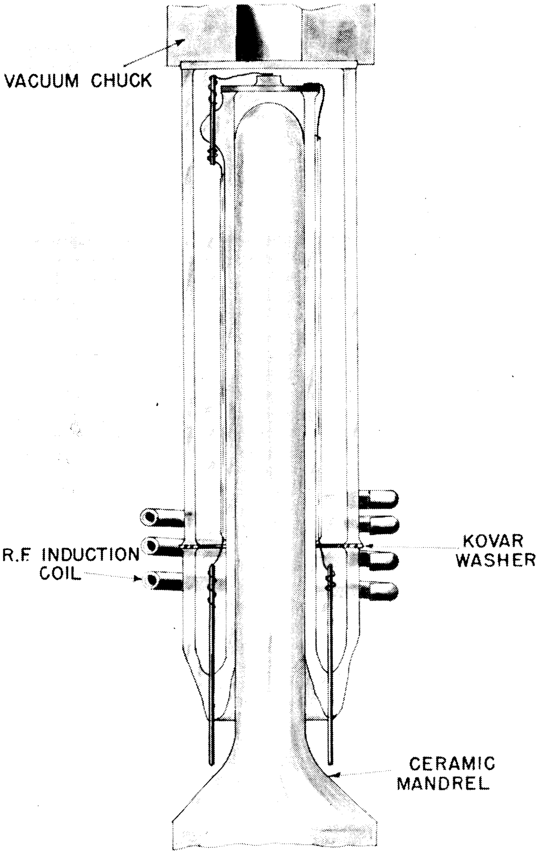


Figure 10
R.F. induction sealing.

inner section. The outer, or top section, containing the sealed-on window rests on top of the Kovar washer and is held clamped in place by means of a vacuum chuck or by a clamp around the O.D. Making certain that the Kovar washer is concentric with the O.D. of the housing, the induction coil is moved to surround the Kovar washer. When the R.F. unit is turned on, the Kovar washer becomes hot enough to soften the glass which is in immediate contact with it. As the glass softens, the fixture holding the top section slides downward due to its weight and executes the seal. The distance of the downward movement is predetermined by adjustment of a micrometer stop. Completion of the seal is determined by observation. The R.F. unit is turned off and the housing is then immediately removed from the setup. To soften the strain introduced from the sealing operation, the housing is positioned on a revolving fixture and a small hydrogen flame is applied to the Kovar washer seal.

Figure 11

R.F. sealing employing an optical comparator.

A. Over-all view. B. Closeup of sealing jig.

Figure 11 shows a sealing setup using an optical comparator. This setup was necessary in a case requiring the detecting elements to be within ±0.002″ of the optical center of the barrel-shaped sapphire. The required close tolerance was accomplished by using a mask arrangement on the comparator screen and by independent manipulation of the inner and outer sections of the dewar housing.

V. CONCLUSION

The foregoing discussion has illustrated how glass technology is applied in specific ways to provide housings with required optical and physical characteristics, and able to electrically accommodate the IR detecting

Figure 12
Various types of glass housings.

elements. Housing configuration varies widely, being influenced by detector type and application. Figure 12 shows a selection of IR detector housings that have been designed and fabricated at Philco's Lansdale Division. This selection represents a wide range of complexity in applied glass technology. Undoubtedly the future will continue to challenge the glassblower's ingenuity to keep glassware development and housing fabrication in step with the rapidly advancing field of infrared.

REFERENCES

1. H. Rawson, "A Method of Sealing Sapphire to Glass," *J. S. I.*, Vol. 28, July 1951.
2. R. P. Chasmar, J. L. Craston, G. Isaacs, and H. S. Young, "A Method of Sealing Sapphire to Glass and Its Applications to Infrared Photocells," *J. S. I.*, Volume 28, July 1951.
3. M. H. Greenblatt, "Sealing a Calcium Fluoride Window to Glass," *Rev. Sci. Instr.*, Vol. 29, p. 738, August 1958.

INFRARED FIBER OPTICAL MATERIALS

L. O. UPTON
American Optical Company
Southbridge, Massachusetts

SUMMARY

A brief description of early work done by research people on the artificial synthesis of infrared optical materials was presented.

The author showed and described a 20-minute colored motion picture film on the distillation principle of glass-making as it applies to arsenic trisulfide glass.

The experimental drawing of infrared transmitting fibers composed of arsenic trisulfide core glass and a related arsenic sulfide cladding glass was also described in a series of 35 mm. colored slides.

HISTORY OF ARTIFICIAL SYNTHESIS OF ARSENIC TRISULFIDE GLASS

We are indebted to Professor Rudolf Frerichs of Northwestern University for his early investigations into the artificial synthesis of infrared transmitting materials. In his experimental attempts to reproduce natural crystals of orpiment (As_2S_3), he found that vitreous material, in other words, glass, resulted from every trial he made. He did succeed, however, in producing material which showed fairly good transmittance in the infrared region of the spectrum.

Later intensive research at the laboratories of American Optical Company resulted in a somewhat purer product but of unpredictable optical properties. Wide variations in visible color ranging from complete opacity to light orange and ruby red were common. Serious problems of homogeneity were indicated by the presence of heavy striae and cords as well as black, opaque inclusions.

No real progress was made until we discovered that during melting, the material seemed to distill and condense on the walls of its borosilicate glass melting container. Samples of the condensate were collected, examined and optically measured. In small quantity, the transparency of the distilled material appeared to be high and its transmission in the infrared proved to be better than that of any previously-made glass.

Work on the proper design of melting equipment by means of which stoichiometric proportions of arsenic and sulfur to produce As_2S_3 could be melted then distilled and condensed several times was completed after many months of unproductive experimentation.

DISTILLING ARSENIC TRISULFIDE GLASS

Now if the operator will start his projector, I will attempt to describe what is going on in our short film, as it was not sound stripped when it was made.

The film was made originally for laboratory record and study only, therefore there is more attention paid to detail than need be for this type of presentation.

The reactor consists of a fused quartz bottle of the opaque grade and is capable of holding a 50-lb. mixture of arsenic and sulfur. The bottle is externally heated in a furnace constructed of resistance heating elements. The elements are wired in three separate circuits so that heat may be distributed as evenly as possible from top to bottom. The furnace shell is a simple insulated steel can. Thermocouples placed at each of the three element levels serve to feed electrical data to each of three controllers which turn the power on and off through magnetic contactors and keep the furnace at desired temperature.

The U-tube, or as we term it, the transfer tube is a resistance-wire-wound opaque fused quartz tube with a tapered neck ground to fit the constricted neck of the reactor bottle. It is surrounded by an insulated shell and is temperature-controlled by its own instrument.

The condenser is a closed-end borosilicate tube inside of a resistance furnace consisting of a steel tube within an insulated steel shell and is also heat-controlled at each of three levels.

A granulated mixture of about 60 weight per cent of arsenic and 40 weight per cent of sulfur is poured into the unheated reactor bottle. A sand seat is prepared to receive the borosilicate glass condenser tube which is placed at the correct depth beside its thermocouple protection sheath. In anticipation of a violent exothermic reaction between the arsenic and sulfur batch ingredients, the transfer tube and condenser are covered with an asbestos blanket. Because the entire operation must be carried out beneath a fume hood, side shields are placed around the furnaces in order to duct the heated air and toxic fumes up the stack.

Within several hours after turning the power on all units, the temperature of the reactor has risen to about 400°C (750°F) and a small blue flame becomes visible in its neck. As the power is increased, the temperature within the reactor rises and a chain-like reaction between arsenic and sulfur particles causes a sudden violent energy release at 550°C (1020°F). This persists for about 3 minutes, after which all becomes quiescent once more as all the batch has reacted and formed molten arsenic trisulfide glass. The protective asbestos blankets are now removed and the transfer tube is fitted to the reactor neck and lowered by its other end into the condenser. The temperature of the transfer tube is held at about 600°C (1110°F) as the reactor temperature is gradually raised to 740°C (1360°F). Raising the reactor temperature, of course, serves to raise the vapor pressure of the arsenic trisulfide within the reactor sufficiently high in order to drive all the arsenic trisulfide in vapor phase from the reactor into the condenser through the transfer tube under its own pressure. Impurities such as occur particularly in commercial grade arsenic metal (graphite, iron scale, mica, silica, etc.) are left behind in the reactor. When it reaches room temperature again, these are removed by means of a suction tube. Owing to the fact that the condenser temperature is maintained at 550°C (1020°F), the arsenic trisulfide vapor quickly condenses on the walls of the glass tube as well as in the cool end of the transfer tube and forms a pool of purified molten glass. The transfer tube is disassembled from the reactor and condenser after condensation is completed in order to make room for insertion of a simply designed fused quartz stirrer. The melt is stirred in the condenser at 120 rpm for several hours at 625°C (1160°F) through a clear fused quartz cover.

The stirrer is removed, the melt is capped and started on its cooling cycle which takes two (2) days.

The borosilicate condenser, owing to its greatly lower expansion coefficient, ($3.2 \times 10^{-6}/°C$) than that of arsenic trisulfide glass ($24.6 \times 10^{-6}/°C$) breaks away from the solidified billet and is discarded. The billet is easily lassoed and removed from the remains of the condenser. The light shows its transparency.

It is subsequently cut into correct lengths and placed within borosilicate glass-covered, aluminum foil-lined, stainless steel molds and is slumped at 325°C (615°F) on polished heat resistant glass into regular rectangular shapes weighing about 15-20 lbs. each.

The transparency and freedom from defects is demonstrated by shining a light through several plates which are about 1½ inches thick.

EXPERIMENTAL DRAWING OF CLAD ARSENIC TRISULFIDE GLASS FIBERS

Because of the strong resistance to devitrification which arsenic trisulfide glass had demonstrated during numerous deliberate attempts to induce it into phase separation, it seemed to be a likely candidate glass for fiber drawing. Cursory experiments were designed to prove that it could be drawn without difficulty. More complex equipment resulted from first trials, then equipment specifically designed to clad the arsenic trisulfide fiber with arsenic sulfide glass of lower refractive index as it was drawn through a specially designed orifice was built and operated. The following figures show the equipment as well as design detail and operation:

Figure 2
Fused quartz tank assembly within furnace.

Figure 1
Method of assembling fused quartz core and cladding tanks.

Figure 3
Fused quartz ball stopper for multiple orifice.

Figure 4
Filling core tank with As_2S_3 cullet chunks.

Figure 5
Filling annular cladding tank with granular cullet.

Figure 6
Covering filled tanks with clear fused quartz cover.

Figure 7
Sketch showing fused quartz melter full of molten glasses.

Figure 8
Experimental spooling of 2 mil clad fibers at 1600 ft./min.

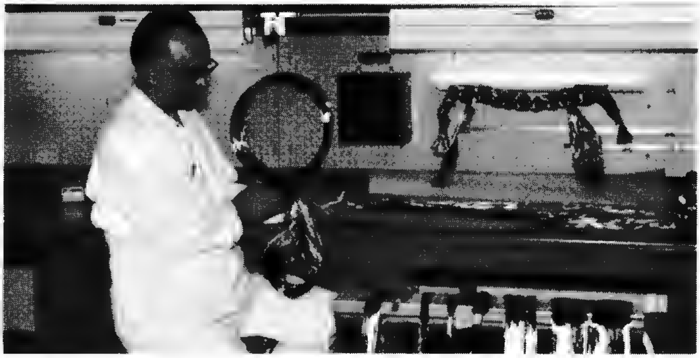


Figure 9
Experimental fiber configurations.

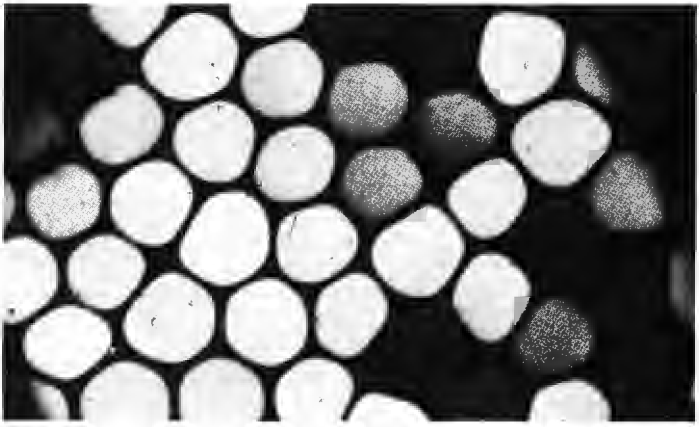


Figure 10
80x magnification of nearly coherent section of fused fiber bundle (10/1 core to cladding ratio).

MOVEABLE COMPONENTS IN HIGH VACUUM SYSTEMS

J. L. A. French
Chemistry Department
University of Toronto
Toronto, Ontario, Canada

Studies of Gas Plasma characteristics in Solar Energy Converters made it necessary to modify the experimental vessel in order to permit controlled movement between components so that optimum Filament to Cathode distances could be studied more economically than with a large number of preset tubes. The mechanism described in this paper was used successfully for the purpose for which it was intended. The principle involved may have other applications in the field of High Vacuum Technique.

There are a number of methods by which limited degrees of freedom may be attained within a vacuum system with widely varying latitudes of control. The more common forms are illustrated in Fig. 1.

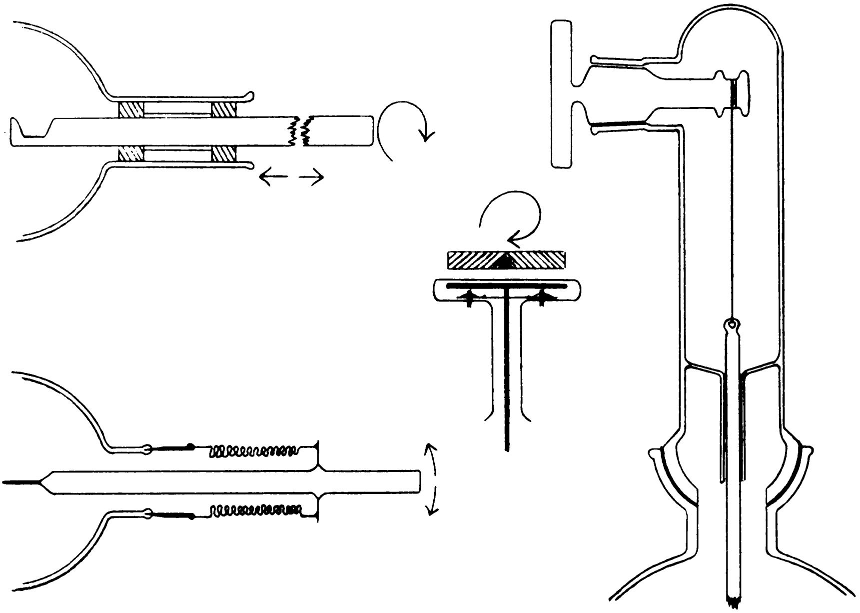


Figure 1

Where slight leaks may be tolerated gaskets of neoprene or rubber may be used, either as O-rings or in the form of Wilson seals. The degrees of freedom are limited to the longitudinal axis as the principal movement, and rotation about its axis as its secondary movement.

Where grease may be tolerated longitudinal movement only may be obtained by raising and lowering a probe by means of a light metal chain, wire or in some circumstances plastic thread, which is wound upon the extended end of a stopcock plug. If provision is made to mount this assembly on to a ball and socket joint limited angular movement may also be obtained.

In certain circumstances no rubber, grease or wax may be used with a system. Under these conditions movement may be effected either by using a corrugated tube, or employing external magnets. In the former method a corrugated brass tube is sealed to the metal end of a Kovar or copper Housekeeper seal with soft solder, the glass side being sealed to the vessel wall. The extremity of the corrugated tube is closed by a soldered metal plate through the center of which is soldered a metal rod which reaches into the vessel on one side and extends externally to form a handle on the other. The flexible corrugated tube permits a limited amount of movement but is not suitable for rotational movement. Where magnets are used on an internal metal plug considerable variety of movement may be obtained. Objects may be moved about the walls of the vessel, or vanes may be turned on spindles. The major drawback is that considerable friction exists between two objects in high vacuum. The writer has seen systems which functioned perfectly in air, but which became jammed when the pressure was reduced to less than 1 mm.

During the course of research work in the field of Solar Energy Converters for the University of Chile, consideration was given to the need to study optimum Filament to Cathode distances with relation to ionization levels within the tubes. In order to avoid having to process a large number of preset tubes with the consequent wastage of time and materials the possibility of working with a movable cathode plate was considered.

During the preliminary work simple diode type electrodes mounted in a borosilicate glass tube 40 mm. in diameter and 110 mm. long were used. Tungsten seals provided external contact, and nickel wires were employed to support a thoriated tungsten filament coaxially mounted within a tubular nickel cathode.

In order to avoid drastic changes in the working characteristics of the tubes it was felt desirable to incorporate in a modified tube only those materials which had been used in earlier studies. Furthermore, the test conditions for the tubes ruled out greases, magnets, etc. which might be used to cause movement. The conditions for testing required heating the tubes in an oven over a temperature range of 120°C. to 200°C. In view of this any mechanism would have to respond to remote impulses and give reproducible predetermined amounts of movement.

The tubes contained excess quantities of cesium both for the performance of the process, and to avoid depletion of the material below its required concentration by absorption into the glass wall, a phenomenon which is well known, but which does not appear to have been subjected to any quantitative studies. The electrode assembly was light weight and in order to avoid difficulties caused by the surface tension of the liquid cesium when the tube is at working temperature the mechanism which must perform the movement must possess a reasonable amount of force.

The ultimate design of the mechanism is shown in Fig. 2. Basically, the principle is that of a metal rod acting against a lever. The system is

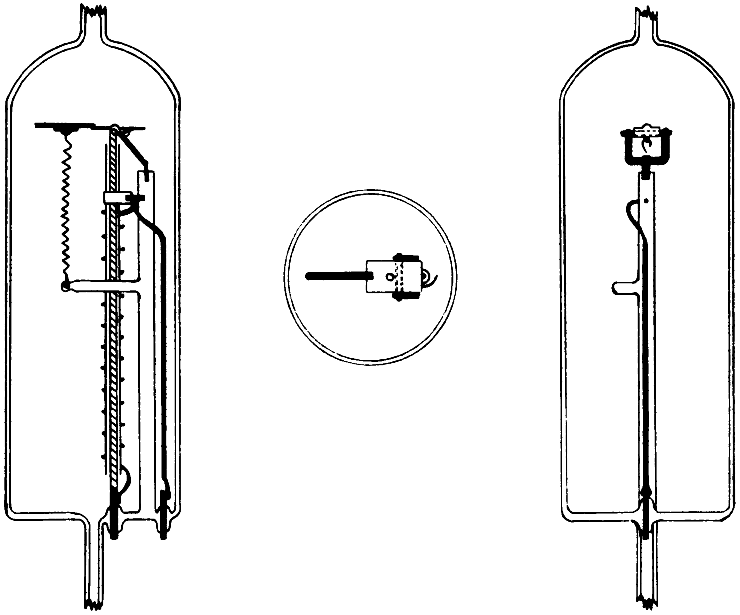


Figure 2

widely used in elementary physics to illustrate linear coefficient of expansion. The amount of force produced in this manner is considerable so that counter pressure in the form of springs could be employed in order to maintain positive control of the moveable components against the adverse effects of the cesium and external vibrations.

The expansion component consists of a 2 mm. diameter nickel rod 120 mms in length mounted on a 2 mm. tungsten rod base seal and surrounded by a silica tube selected to give an easy sliding fit. This tube serves as a support for the nickel heating coil which is wound on to it and adds rigidity to the nickel rod inside it. A glass rod 6 mm. in diameter is located parallel to the silica tube with a separation of 10 mm. in order to avoid excessive surface temperatures, the lower end of the rod being sealed into the base of the tube. The upper end terminates 10 mm. below the top of the thick nickel rod which should protrude 3 mm. beyond its surrounding silica sleeve. At this point a tungsten rod is sealed into the side wall of the glass rod and reaches across to the silica sleeve and forms a bridge between the rod and sleeve so as to reduce movement between them. The joint between the sleeve and the tungsten support is a nickel collar pressed around the silica and spot welded to the tungsten. The nickel heater is made out of 28 BS wire and is 80 cms long being wound so that it is distributed evenly along the length of the silica sleeve, the top end being welded to the tungsten support and the bottom end to the base electrode used to retain the nickel expansion rod. A nickel wire 22 BS connects the top of the heater to a base pin adjacent to the one used as a support.

In order to support the moveable components of the mechanism a 2 mm. diameter tungsten stub is sealed into the top of the glass support rod, to this stub is welded a U-shaped nickel component 2 mm. in diameter with arms 15 mms long and 10 mms apart. The angle of attachment is such that the upper ends are immediately above the expansion rod within the silica sleeve, and are at right angles to the plane of the sleeve and support rod.

A flat strip of nickel .5 mm. thick, 10 mm. long and 9.5 mm. wide is mounted on a 1.5 mm. diameter smooth tungsten rod 12 mm. long so that it pivots easily across its center. A small concave depression located 1 mm. beyond the hinge bearing and centrally located in the hinge serves as a bearing point for the top of the expansion rod, the end of which should be spherical. The hinge is located so that it is horizontal to the expansion rod and the tungsten bearing welded to the open extremities of the U-support so that the top of the expansion rod is located in the concave depression in the hinge. It is advisable to weld one side first and adjust the component so that there is a minimum of transverse movement before welding the second side.

An arm to act as a lever and to the extremity of which may be attached a cathode plate or other device is welded on to the edge of the hinge. In this case a nickel rod 1.5 mm. diameter and 25 mm. long was used. At approximately 12 mm. from the fulcrum a hook is attached and a light tungsten spring placed between it and a convenient anchor point some 50 mms below it. This spring ensures that the hinge is firmly in contact with the top of the expansion rod at all times.

The center to center distance between the fulcrum of the hinge and contact point of the expansion arm on the one hand, and the length of the object support arm on the other will determine the magnitude of movement that may be achieved without excessive temperature being applied to the expansion rod. Due to limitation imposed by the tube envelope the contact to fulcrum distance was made as small as physically possible.

In practice the heater voltage was kept below 2.5 volts in order to avoid conflict with the tube characteristics. By careful calibration it was found possible to change filament to cathode distances in steps of .5 mms. over a range of 8 mms. The basic principle involved is very simple, and no doubt will have other applications. The mechanism may be constructed from other materials than those required in the sophisticated tube under discussion.

The main advantage lies in the possibility of maintaining remote control of the mechanism, coupled with which the motivating force is adequate to overcome frictional drags in high vacuum.

In conclusion the writer would like to acknowledge the assistance rendered him by the A.S.G.S. in completing this paper in the limited time available to him and to thank the University of Chile for providing funds and materials to carry out this work.

QUALITY CONTROL TECHNIQUES IN APPARATUS PRODUCTION

JOHN V. ARMSTRONG
Fischer & Porter Co.
Warminster, Pa.

The greatly increased precision demanded of manufactured parts has been accomplished by the need for better methods to measure, specify, and record it. Thus it was almost inevitable that *Statistics,* the *so-called science of measurement,* would become one of the most valuable techniques used in the Quality Control function.

Statistical Methods have had a long and rocky road to the general acceptance that they now enjoy in industry. Opposition to them was due, in part, to the natural resistance met during the introduction of any new method.

In part, it was due to the shopmen's fear of the mathematical symbols which seemed to cloak industrial statistics with an air of mystery. In part, it was due to the overabundance of technical statistics and the underabundance of practical administrative applications that characterized the literature which reached industrial management. In part, it was due to the simple fact that the formal education of many graduate engineers overlooked concentration of this subject. Today, there is a growing wealth of material on the practical aspects and theoretical details of industrial statistics. The statistical terminology and mathematics have been reduced to simple arithmetic and algebra for general use. A surprisingly large number of industrial employees have been trained in these methods.

The victory of statistical methods in industry really represented a compromise between "pure" statistics and the practical realities of industrial situations. Statistical methods, as actually practiced in Quality Control, do not represent an exact science. Their character is strongly influenced by Human Relations factors, technological conditions, and considerations of cost.

A plant Quality Control Program may, for example, be faced with the problem of choosing between two sampling tables. One table may be quite precise statistically but may be difficult for shop people to comprehend. The other table may not be so precise statistically but may be much easier to administer. It would be quite typical for the plant to select the latter table.

Probably more important than these methods themselves has been the impact upon industrial thinking of the philosophy they represent. The "statistical point of view" resolves essentially into this: variation in product quality must be constantly studied within batches of the product; on processing equipment; between different lots of the same article; on critical quality characteristics and standards; in regard to pilot runs of a newly designed article. This variation can be best studied by the analysis of samples selected from the lots of products or from units produced by the processing equipments.

This point of view, which emphasizes the study of variations, has had a significant effect upon Quality Control activities wherein the actual statistical methods themselves are not used. The study of variation that is recommended has begun to go beyond the bounds of Quality Control itself into other administrative areas like time study, safety engineering, and personnel administration.

Five (5) statistical tools have come to be used in the Quality Control jobs. They are as follows:

1. Frequency distributions
2. Control charts
3. Sampling charts or tables
4. Special methods
5. Reliability prediction

Some understanding of these tools is useful for full technological comprehension of Quality Control. We are limited in time, so we shall discuss those that can be most useful to you.

One of the characteristics of modern manufacturing is that no two pieces are ever exactly alike. The variations may be small—as in the case of gage blocks, which have been guaranteed to two-millionths of an inch. Whether large or small, variations exist in parts manufactured in all production processes whether they be hand lathes, blanking presses, annealing furnaces, or painting machines.

Some variations are so great that they are immediately shown by modern measuring equipments. Other variations are so minute that suc-

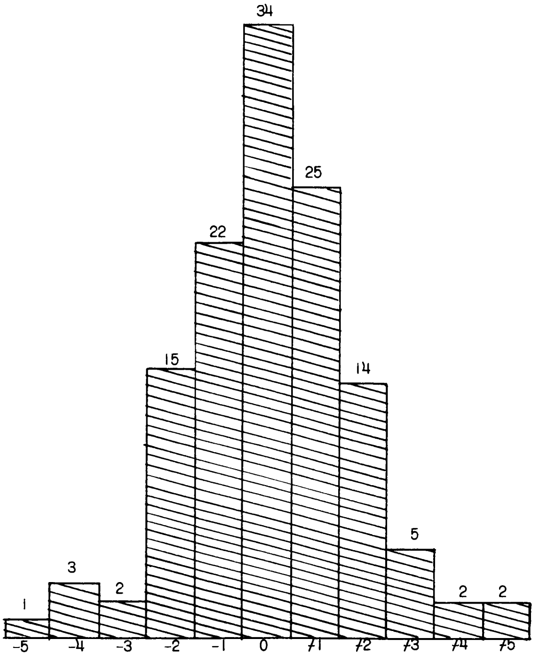


Figure I

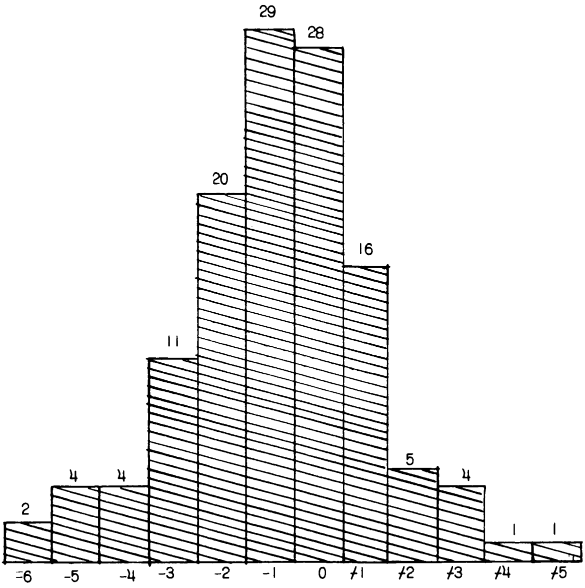


Figure 2

cessive readings on measuring equipment will reflect primarily the variation of the measuring equipments themselves rather than that of the parts.

Among the types of parts' variations, there are three classifications useful for analytical purposes. They are:

1. Variations within the part itself.
2. Variations among parts produced during the same period of time.
3. Variations among parts produced at different periods of time.

There are many factors that contribute to any or all of these variations. Among them are tool wear, bearings that loosen, machine vibrations, faulty jigs and fixtures, poor raw material, careless or untrained operators, and even weather changes.

Industry has long recognized the inevitability of these variations. It includes, on drawings and specifications, tolerances which designate the permissible deviation from the standard shape, thickness, color and size.

With all assignable causes of deviation removed from a process, let us then look at a normal recorded FREQUENCY DISTRIBUTION Fig. 1). Here we see the variation inherent in the process. This particular distribution is considered normal. Here is a FREQUENCY DISTRIBUTION CHART on the same part recorded the following day (Fig. 2). The change is quite apparent. The overall length nominal has shifted down. Immediate action can be taken, for here the reason was quite apparent—the stop on the lathe moved.

As more and more data is gathered for the frequency distribution charts, we can go still further. *The control chart.* The limits for the control chart are set by the operation itself; a specification limit is usually established by a human being—often the design engineer—who takes into account factors external to the operation.

Now let us devote a little time to the mechanics of setting the control limits. The Quality Control Engineer calculates the control limits by using the square root of the variance, known as the *standard deviation or* SIGMA.

The Standard Deviation expresses dispersion in the form of a single number, which is also known as the *"root mean square deviation"*. It is found by noting the deviation of each item from the arithmetic mean, squaring each deviation, adding these squared deviations, dividing by the number of observations, and taking the square root.

This then is the Standard Deviation or SIGMA. Plus or minus one Standard Deviation will guarantee us that 68.27 per cent of the parts will be within these limits. However, no Company can operate with that kind of a yield. We must do better. Therefore, we multiply the Standard Deviation by 3 and set our control limits. As long as our production samples fall within these limits, we are assured that 99.73 per cent of the parts will be acceptable.

A demonstration of this would be the height of people. The average height of an adult is 69 inches, or 5 feet 9 inches, with the Standard Deviation being 2 inches. Therefore, 68.27 per cent of this group is between 5 feet 7 inches and 5 feet 11 inches. Because we want a larger majority to benefit from this talk, we will apply the three standard deviation rule. Now the limits are 5 feet 3 inches and 6 feet 3 inches. QUESTION TO THE FLOOR: *How many here are shorter than 5 feet 3 inches? How many are over 6 feet 3 inches?* (If any, there is either something wrong with our process or there are some rejects in the group from Brand X.)

Statistical Quality Control is the stepping stones to better Quality, lower costs, and increased production.

PRACTICAL GLASS CLEANING

ROBERT M. TICHANE
Technical Staffs Division
Corning Glass Works
Corning, New York

INTRODUCTION

Recent electronic and vacuum device technologies have shown a strong trend toward higher and higher quality requirements. To meet these requirements the device maker must be supplied with raw materials of superior purity and cleanliness. One of the most important aspects of glass in devices is the surface quality; hence the subject of this paper will be the practical problem of obtaining and maintaining clean glass surfaces before, during, and after normal forming processes. Classifications have been made according to contaminant type.

ORGANIC CONTAMINANTS

First let us look at organic contaminants. Their presence must be immediately suspected whenever a glass surface is found to be non-wetting in the atomizer or water break test described by Feder and Koontz[1]. Statistically, such a high percentage of cases of non-wetting glasses are due to organic materials that it is practical to consider them the sole cause of non-wettability except in unusual circumstances.

The easiest way for a glassblower to get rid of organics is by heat treatment, either burning them off in an open flame or oxidizing them in a furnace in air. This will normally succeed except in the case when the organics are combined with inorganics, as in the case of silicones, soaps, greases, or physically combined organic-inorganic mixtures.

A familiar example of this is the finger print which leaves its permanent mark on heated fused quartz tubing (Fig. 1). If the finger print were only organic in nature it would be a simple matter to burn it off in a flame. However, it contains alkali salts from the skin also, and these are diffused into the glass by heat, where they catalyze devitrification.

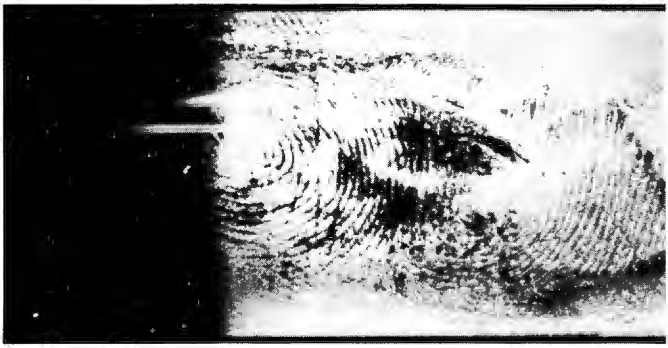


Figure 1
A fingerprint burned into a fused quartz surface (3X)

Figure 2
A silicone layer burned into a soft glass surface (1X)

Another technique for removing organic films is the use of suitable solvents such as ethyl alcohol, acetone or trichloroethylene. These may be applied in a number of ways ranging from sponging with a clean cloth to vapor phase degreasing, always exercising care to avoid fire or toxicity hazards. In the case above, alcohol can be used to remove finger marks on fused quartz. Very fine technique requires the use of ultra-pure, ultra-clean solvents.

When the organic film is particularly tenaciously held, as in the case of silicones, it becomes practical to remove this layer by stripping a layer of glass off beneath the organic matter and then floating off both the film and glass layer. This can usually be done by immersing the sample in a solution of dilute (1-5%) hydrofluoric acid, and then flooding the container with deionized water to float off the removed film. By keeping the hydrofluoric acid hot and dilute, formation of precipitates is minimized.

The type of difficulty one encounters with burned in silicones or greases can be seen in Figure 2. This is a piece of soft glass, silicone coated and softened in a gas flame.

INORGANIC CONTAMINANTS

Turning to inorganic contaminants, the most commonly observed condition is due to weathering. In Figure 3 we see an electron micrograph of a weathered soda-lime glass surface with its collection of alkali carbonates and sulfates, formed by the reaction of the glass with moisture and gases from the atmosphere. Fortunately, borosilicate glasses are much more resistant to the elements, as can be seen in Figure 4, which is a severely exposed piece of this glass type.

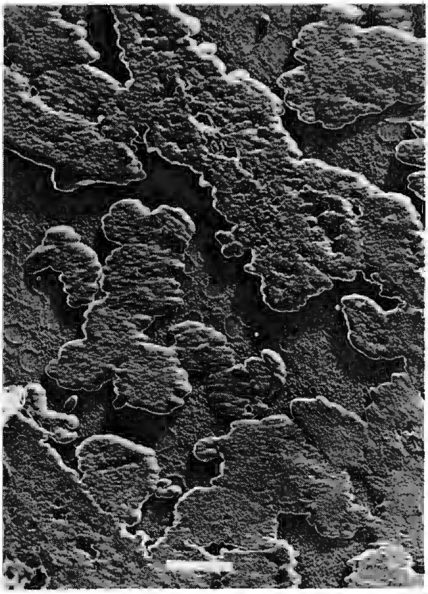


Figure 3
A weathered soda-lime
glass surface (10,000X)

Figure 4
A weathered borosilicate
glass surface (10,000X)

Figure 5
A washed sample of weathered soda-lime glass (5,000X)

Luckily, weathering products can usually be removed simply by washing or fire polishing[2,3]. Figure 5 shows a view of the soda-lime glass sample in Figure 3 after a water wash.

Occasionally weathering will change a surface permanently, either by leaving an insoluble deposit, or by corroding the outermost layer of glass. Pieces of window glass which have been stored for years, close together and in variable humidity conditions will often be found to be permanently scarred as can be seen in Figure 6.

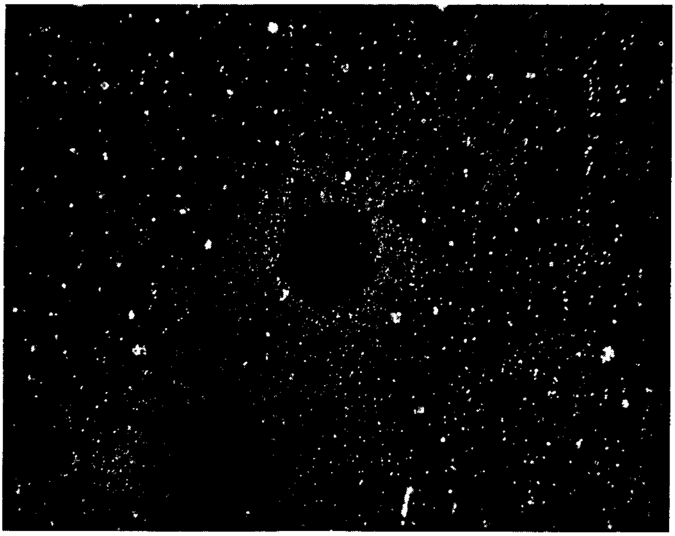


Figure 6
A permanently scarred window glass surface (150X)

There is a group of items that should be mentioned now under the general heading of: *Cleaning The Unseen.* Several materials can contaminate glass without being easily visible or detectable.

One case in point is the fluoride ion which is left as a layer on the glass surface after hydrofluoric acid cleaning. Unless one were prepared to examine this glass for outgassing in a mass spectrometer, it would be difficult to recognize this contamination. Yet, in a vacuum tube device containing an oxide coated cathode enough fluoride might be released to affect electron emissivity adversely[4].

Similarly an alkaline film can be present on glass after heat treatments if the glass contains alkali ions. And the alkaline film may do such things as form metal-alkali alloys under strongly reducing conditions or cause high and erratic electron emission from cathodes in electronic devices.

A particularly deceptive film is the one left on glass by alkaline baths such as sodium hydroxide or carbonate solutions. These are deceptive because while the glass is wettable and apparently clean after treatment, it is actually grossly contaminated with a hydrophilic alkaline layer. Figure 7 shows an electron micrograph of a soda-lime glass after treatment with hot 1% sodium hydroxide solution. To get a clean surface here one would need to wash thoroughly with an acid such as a hydrochloric acid. The most thorough water rinse will not remove the alkaline film.

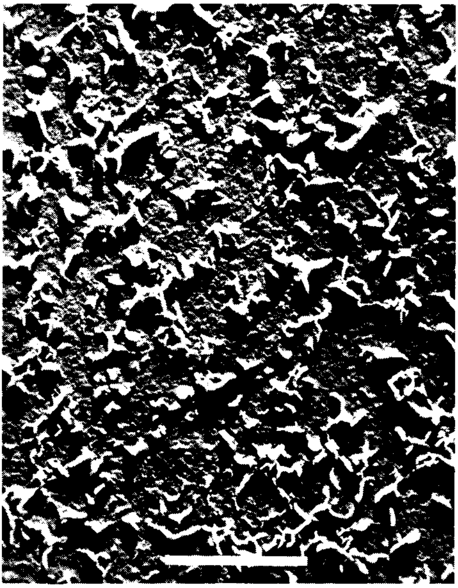


Figure 7
A soda-lime glass surface after 1 minute in 1% sodium hydroxide (25,000X)

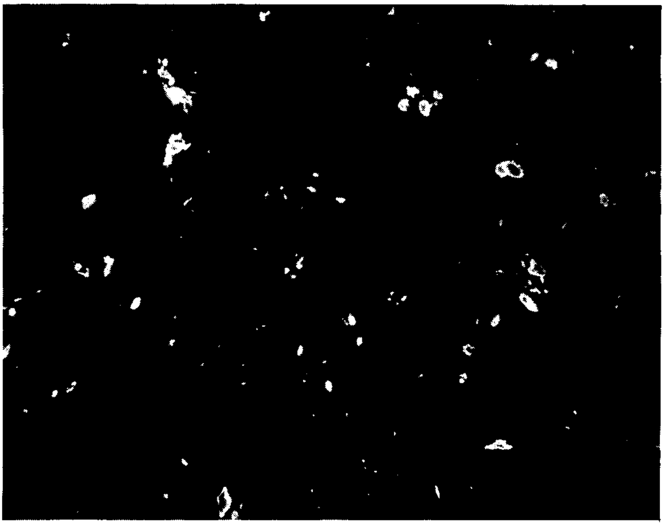


Figure 8
A polished glass surface with rouge trapped in grinding pits (150X)

SURFACE DEFECTS

Many imperfections fall under the heading of physical defects. One example of this is found when flat glass is not ground and polished correctly so that grinding and scratch marks can be detected either visually with oblique or edge lighting or microscopically using darkfield or incident light. Frequently these surface defects are filled with polishing powder and in these cases a coloration can be noted on the glass when this is observed in a glancing light beam. The example in Figure 8 shows an improperly finished piece of flat glass with rouge trapped in the grinding pits.

Two other physical defects are glass chips and grinding wheel residues that are held very tenaciously to glass either by electrostatic attraction or by adhesive, bonded-wheel residues.

It is very important to remove these materials quickly from the glass when they are less tenaciously held and before they have a chance to cause scratch damage. It is helpful to use ultrasonic cleaning for this, but sometimes careful brushing or a clean air blast will work.

ROUGHENING OF GLASS

Perhaps it would be permissible to digress momentarily from cleaning and mention roughening techniques, since it is sometimes as difficult to roughen a glass surface as it is to smooth it. Grinding and sandblasting are certainly obvious techniques, but they are limited in applicability because of their weakening of the glass surface and because of the difficulty of applying them to irregular or hard-to-reach areas. A chemical frost is often needed and for soda-lime or lead glass the classical Pipkin[5] frost solution may be used, or a simple slurry made up of ammonium

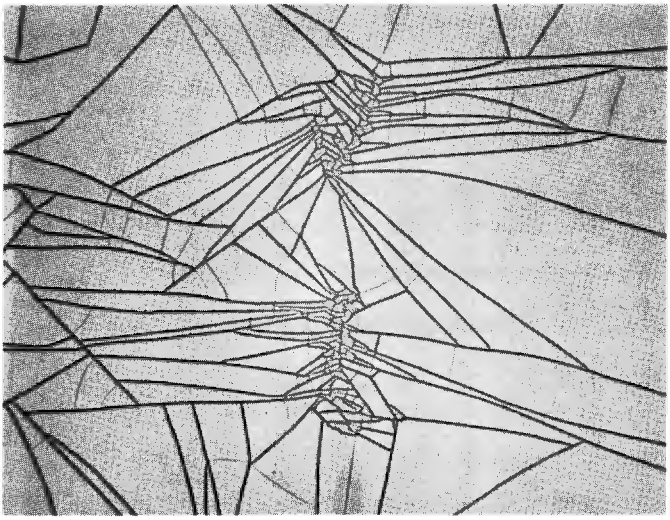


Figure 9

Surface crazing in a high barium glass treated in hydrochloric acid (200X) chloride and 48% hydrofluoric acid. When warm, these solutions will produce a satisfactory frost in less than a minute on soft glasses. Unfortunately it is difficult to obtain a consistently uniform frost on borosilicate and high silica glasses and for them mechanical roughening may be the best technique.

Hydrofluoric acid by itself will smooth glass surfaces if no precipitates or irregularities are present. A hot dilute solution will accomplish this purpose best. The tendency for precipitates to form will naturally increase as the concentration rises and the temperature decreases. Addition of strong nitric acid will help suppress precipitation. Even with precipitates, however, smoothing can be accomplished if the precipitates are promptly washed off. For example, witness the effect of concentrated HF and concentrated H_2SO_4 in the so-called polishing acid used to remove grinding marks from soft lead glasses[6]. A scum is formed on the glass, but this is quickly washed off before frosting or staining can occur.

Overcleaning is not a subject to be ignored just as over-heating of glass cannot be neglected. The principal danger is in leaching the surface layers of soluble materials such as alkalies, alkaline earths, boron or lead. For instance, a high barium glass can have its surface completely depleted and destroyed by a ten-minute treatment in hot dilute acid as can be seen in Figure 9.

CONCLUSION

In summary this can be said: One should be aware of the great capabilities of both simple detection and simple cleaning techniques. Only when these fail should more complicated processes be used. Make intelligent and full use of the eye as a detection instrument before resorting to electron microscopy or mass spectrometry. Similarly one should try cleaning with a puff of clean air or deionized water before resorting to ultrasonic cleaning or boiling hydrofluoric acid.

REFERENCES

1. Feder, D. O. and Koontz, D. E.—"Detection, Removal and Control of Organic Contaminants in the Production of Electron Devices," ASTM Special Technical Publication #246, p. 40, 1958.
2. Tichane, R. M. and Carrier, G. B.—"Microstructure of a Soda-Lime Glass Surface," *J. Am. Cer. Soc.* 44, p. 606, 1961.
3. Tichane, R. M.—"Cleaning Processes for Borosilicate Glass," *Am. Cer. Soc. Bull.* **42**, p. 441, 1963.
4. Kern, H. E. and Graney, E. T.—"Thermionic Emission from Oxide Cathodes as Related to Glass Envelope Composition," ASTM Special Technical Publication #246, p. 167, 1958.
5. Pipkin, M.—"The Inside Frosting of Incandescent Lamps," *Ind. & Eng. Chem.* **18**, p. 774, 1926.
6. Meth, I.—"Glass Polishing Solution and Method," U. S. Patent 1, 777, 321.

GLASS GRINDING

D. T. TAURONE
Norton Company
Worcester, Massachusetts

In regard to the grinding of glass, your range of interest is no doubt quite wide. There, I will discuss several of the different grinding operations.

Three specific phases of glass grinding will be covered:

1. the abrasive wheels
2. several actual operations
3. some operating suggestions

Because of the hardness of glass it is necessary to use abrasives to grind, cut and finish this material to shape, size and surface finish.

The abrasives used are bonded abrasive wheels, coated abrasive sheets and loose abrasives.

The bulk of the glass grinding operations, and the most complicated are performed with abrasive wheels. This paper will be concerned with glass grinding with bonded abrasive wheels.

The abrasives used in bonded wheels for grinding glass are: 1, aluminum oxide; 2, silicon carbide; and 3 diamond.

Many of you are familiar with aluminum oxide and silicon carbide wheels which have been used for generations. Not so many are perhaps familiar with diamond wheels.

We will discuss all three types. However, one intention of this paper is to point out the features and advantages of diamond abrasive wheels for many of the glass grinding operations.

A grinding wheel consists of two main materials.

First, the abrasive particles that actually do the cutting.

The second ingredient is the bond that holds the abrasive grains while they cut.

This close up view shows a handful of vitreous bond before being mixed with the abrasive.

This sketch illustrates the controlled spacing of the abrasive particles which are separated by bond posts.

The relative volumes of bond and abrasive determine the hardness or grinding grade of the wheel.

Here are aluminum oxide and silicon carbide wheels. Such wheels are bonded with vitrified, or resin or rubber bond.

Vitrified is by far the most common.

These are some typical diamond wheels. Because of the high cost of diamond wheels, only a thin layer of the wheel contains diamond particles. Note the wheel on the right has a marking that includes a fraction of 1/8″. This tells us that the depth of the layer of diamond is 1/8″.

In this case the diamond is on the periphery of the wheel and the 1/8″ is a radial measurement.

Diamond is bonded with metal, or vitreous or resin bond. Metal is most widely used for glass grinding.

In order to get a clearer picture of wheel specifications, let's examine two typical wheel markings.

19A	220	—	0	11	VBE
ABRASIVE TYPE	SIZE		HARDNESS	SPACING	BOND TYPE

This first wheel marking is an actual popular wheel for grinding the edges of lens.

On the left, in the first position is indicated the type of abrasive. 19A is one of the aluminum oxides.

In the second position is the grit size, in this case 220.

Next is a letter to designate the hardness grade. A letter further toward the end of the alphabet designates a harder wheel.

The fourth position is a number to indicate the spacing of the bond and abrasive.

The last position on the right shows the bond type. Here we have a vitreous bond.

D	100	—	N	100	B	$\frac{1}{8}$
DIAMOND	WHAT SIZE		HOW HARD	HOW MUCH	WHAT BOND	HOW DEEP

Here is a diamond wheel marking. On the left is shown the type of diamond. In this case regular natural diamond.

The second position is the grit size of the diamond.

The third position is the grade hardness letter.

The 100 indicates the diamond concentration which we'll go further into in a moment.

The 5th position shows the bond type. In this case B for resinoid bond.

Note this wheel marking differs from the aluminum oxide marking in that this one shows the concentration, or in effect the volume of diamond. It also shows the depth of the diamond layer at the right of the marking— in this case $\frac{1}{8}''$.

The concentration of a diamond wheel is important and should be explained further.

In this case we show 100 concentration but the normal concentrations are 100 or 75 or 50 or 25.

This illustrates the relative volumes of diamond, in a given wheel, as the concentration varies from 25 to 100.

A 100 concentration Norton diamond wheel is made to a formula— calling for 72 carats of diamond per cubic inch of the diamond section of the wheel.

50 concentration would be exactly half that— or 36 carats per cubic inch.

25 concentration would be 1/4 of 100 or 18 carats per cubic inch.

Actually there is no industry standard for concentration and it will be found that some manufacturers of diamond wheels vary.

In the course of a talk of this duration it cannot be expected to learn how to select the complete wheel specifications for the various applications. Each job should be considered alone.

However, to start you in the right direction toward selecting wheels we will discuss further the most important ingredient in the wheel—the abrasive.

Aluminum oxide and silicon carbide were used long before diamond wheels were developed. They are still used extensively today.

The first bonded diamond wheel made in the U.S. was manufactured in the early 1930's. The first wheel using manufactured diamond was made only 5 years ago.

However, both natural and manufactured diamond are excellent for grinding glass.

The advantages of using aluminum oxide or silicon carbide abrasive are, first, lower initial cost.

Second, these abrasives can often be used on less expensive equipment or on older machines that are already on hand which might not be satisfactory for diamond wheels.

Third, these abrasives, especially aluminum oxide, give a more nearly transparent finish on the glass.

The advantages of using diamond are four:

One, longer life. Diamond wheels last many times longer. Therefore, less wheel changes or machine adjustments are required.

Two, grinding wheel cost and total grinding cost are usually lower. Certainly they are lower for production grinding.

Third, because diamonds are harder they cut and grind many times faster.

Fourth, diamond wheels hold their size and shape for a long time. Therefore, less machine or wheel adjustments are required to maintain shape and tolerances on the glass.

It is indicative to note that new machines being designed for production grinding of glass are more and more being designed for and equipped with diamond wheels.

The rapid growth of glass as an industrial material and also the development of harder and difficult to work types of glass have required the increasing switch to the fastest grinding abrasive which is diamond.

As a matter of interest here is a picture of diamond bort. This diamond has the same chemical and physical properties as the diamond used for jewelry.

However, bort diamond, which means diamond for industrial use, has discolorations which make it unsuited for gems.

Now that we have a background on abrasive wheels, let's go on to some of the operations.

In production work, holes are drilled in glass with diamond core drills.

Figure 1
Drilled hole

After drilling this 1/4″ hole the machine was stopped to show the drill more clearly. The coolant would be forced through a hole in the adapter, then through the inside of the drill.

Note the core has been placed on the glass.

The smallest drill shown is 1/4″ in diameter. Core drills are used to grind a variety of hole sizes in glass.

Figure 2
Core drills

Popular applications would be mounting holes in mirrors, automobile windows, and various tableware.

Pencil Edging is the grinding of a radius on the edges of glass. The most common examples are on your automobile door windows.

Figure 3
Pencil edging wheel and glass.

The wheel is shaped to grind the radius. The black line represents the center line of the spindle on which the wheel is mounted.

The glass is passed along the shaped periphery of the diamond wheel.

This close up shows the ground pencil edge on a pane of glass from a jalousie window.

Figure 4
Pencil edged glass.

Other popular edging operations would be mirror beveling and seaming.

Lens grinding involves grinding the radius on the surface of the lens and grinding the contour on the edge of the lens.

Both opthalmic lens and lens for optical instruments are ground in the same manner.

Figure 5
Lens generator.

This shows a typical set up for grinding a convex curve. The machine and coolant are shut off for visibility.

Figure 6
A large lens generator.

In this case the coolant passes down through a hollow spindle and through the inside of the diamond generating wheel.

The spindle can be tilted to different angles in order to grind different radii with the same diamond wheel.

Here we see a special #11 Blanchard grinder about to use a 10″ diameter diamond wheel to generate a concave radius.

Figure 7
A Blanchard surfacing.

This is a typical surfacing operation. It shows how many small parts can be grouped in a chuck for surface grinding.

Figure 8
Cutting-off.

This illustrates a glass rod being cut-off with a diamond saw.

Other popular cut-off jobs are cutting tubing, diode jackets, bottles for surface examinations and certain plate glass cutting.

Now that we have discussed the abrasive wheels, and some of the major operations, we should now consider some general guides for efficient and economical use of diamond grinding wheels.

The major variables to consider are wheel speed, feed rate, feed pressure, coolant, work holding, and wheel dressing.

The optimum wheel speed varies in glass grinding. However, here are some general recommendations.

Diamond wheels should run at least 3500 SFPM but preferably between 5000 and 6000 SFPM. Cutting off saws should operate higher—around 7000 SFPM.

The point to remember in feeding the wheel through the work, or vice versa, is do not dwell. A rate of feed that is too slow will load the wheel with glass particles and hinder its ability to cut. One should feed as fast as possible without overloading the machine or the wheel. If the glass chips excessively, it could mean an excessive feed rate.

The rule for the correct pressure between the wheel and the glass is similar to the rule for feed. The pressure should be sufficient to keep the wheel working—that is, cutting. However, excessive pressure will cause glass chipping.

Coolants are a must in glass grinding. Grinding dry will burn, chip or break the glass. Of course certain light work such as hand mitering must be done dry, or nearly so, so that the work can be seen.

The functions of a coolant are,

1, to keep the glass and grinding wheel cool. This prevents burning and permits faster grinding.

2, to keep the wheel face clean. A clogged wheel face will cut slowly or not at all.

3, to wash away the swarf

4, to give a better surface finish

A good heavy flow of coolant is recommended, and it should be directed to hit the area of contact between the glass and the wheel.

Actually plain water is satisfactory as a coolant. However, soluble oil is normally mixed with water to give a better surface finish and to prevent machine rust.

The ratio of oil to water is usually 1 part oil, by volume, to 50 or 75 parts of water.

The coolant should be kept clean by filtering or by using an adequate settling tank.

Firm holding of the glass is important to minimize chipping. The glass should not be allowed to move or vibrate.

In the case of cutting off, if chipping is to be minimized, the glass should be supported underneath by a material that can be cut into with the abrasive saw. Examples for back up materials are fiber board, ceramics, wax, plaster of paris and of course glass.

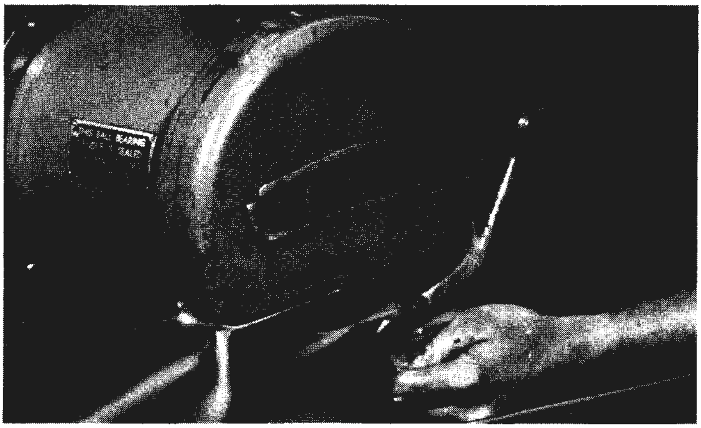


Figure 9
Dressing.

Dressing is the operation in which the face of a grinding wheel is cleaned to restore the proper grinding action.

If the face of a wheel becomes excessively loaded with glass, or glazed, it should be rubbed for several seconds with an abrasive stick—while the wheel is running at its regular grinding speed.

Some wheels require no dressing throughout their entire life. Often a wheel needs to be dressed several times a day. If the proper wheel is being used it should not be required to dress more than a couple of times a day.

Any talk on grinding wheels would not be complete without a word on safety.

Rather than try to point out various safe operating procedures it will suffice to show these various booklets on this subject and to stress that anyone using abrasive wheels should be familiar at least with the booklet shown in the upper right. It is the "American Standard Safety Code for the Use, Care and Protection of Grinding Wheels" as approved by the American Standards Association. Incidently, it was just revised last February.

SUMMARY

And now for a very brief summary:

Diamond wheels should be used for production grinding. They grind faster and are usually more economical.

The optimum diamond wheel speed is normally 5 to 6000 SFPM, but for cutting off saws it is around 7000 SFPM.

The feed and pressure should be sufficient to make the wheel work, but not enough to overwork or stall the motor.

The coolant, usually a soluble oil, should be a good heavy flow directed at the area of contact between the wheel and the glass.

The glass should be held securely.

GLASS RESINS—A NEW MATERIAL FOR VACUUM SEALS AND OTHER USES

ROBERT E. MARTIN
Owens-Illinois Glass Co.
Toledo, Ohio

INTRODUCTION

One of the most active areas in polymer research today is the development of new high temperature resins and adhesives. In addition to thermal stability, these materials are generally expected to resist chemical attack and to be dimensionally stable. It is relatively simple to figure out which chemical compositions and structures should give these properties. However, converting the theories into practice has so far proved to be both difficult and costly. As a result, there are no commercial polymers available today with unlimited service lives much above 200°C. in air. Even the best of these tend to soften and discolor at elevated temperatures.

There are two major approaches, both receiving about the same amount of attention, being used to synthesize high temperature polymers. In one method, polymer chains are formed by linking cyclic organic compounds. A few of these polyaromatics are beginning to appear on the market, but it is too early to say much about their performance characteristics. The second approach is to eliminate all carbon to carbon bonding in the polymer backbone. With the exception of the silicones, none of these so-called inorganic polymers has been made in a useful form. Owens-Illinois has been interested in this general area for many years, and has recently developed a new family of inorganic polymers called Glass Resins.

Because Glass Resins are based on an alternating silicon-oxygen system, they can be classed generically as silicones. However, unlike conventional silicones, they can be cured to crystal-clear thermosetting materials without the use of fillers and modifiers. As a result, some of them contain better than eighty percent silicon and oxygen. This leads to physical and chemical properties generally superior to those of commercial silicones. By varying the type and relative amounts of starting materials, it is possible to make hundreds of compositions, each with different properties. It is, therefore, possible within limits to tailor-make Glass Resins for specific end use applications.

GENERAL DESCRIPTION OF GLASS RESINS

As first prepared, Glass Resins are water-white viscous liquids, usually dissolved in ethanol. The viscosity can be varied widely by adding or removing solvent. In this state the resins can be used as coatings, sizes, adhesives, and laminating resins. A simple heat treatment of these soluble thermoplastic resins converts them to hard thermosetting materials which are no longer soluble. The length of time required for this final cure depends on the thickness of the film and on the resin composition. Metal to metal, glass to metal, and glass to glass seals have been made in this manner. Glass Resin castings can be made in a variety of shapes and sizes. There appears to be no practical limit to the size of specimen that can be cast. The details of forming and handling procedures are presented later in the paper.

All the property data which follows is for only one Glass Resin composition which contains no fillers or modifiers. The values should, therefore, be taken as general, rather than as specific. There is no doubt that any or all of them can be improved by the incorporation of fillers, by compositional changes, or by some combination of these.

OPTICAL PROPERTIES OF GLASS RESINS

A one-eighth inch thick specimen of Type 100 Glass Resin transmits ninety-five percent of 360-700 millimicron radiation at room temperature. Its refractive index, n_D^{20}, is 1.4965. The optical dispersion is 0.0242. Refractive indexes for other resins have ranged from a low of 1.420 to 1.503. There are indications that even higher values may be possible. Recently, Type 650 Glass Resin was developed to fill the need for good ultraviolet transmission. This material has a cut-off at 194 millimicrons, and transmits approximately fifty percent at 230 millimicrons. Only fused silica, quartz, and certain special optical glasses have comparable values.

ELECTRICAL PROPERTIES OF GLASS RESINS

Glass Resins have good dielectric properties at room temperature and excellent properties at elevated temperatures. The values are roughly equivalent to Kel-F or the steatites. For Type 100 Glass Resin at 25°C., the dielectric constants are 3.77 and 2.91, at 60 cps and 1 Mc, respectively. For the same conditions, the dissipation factors are 0.0030 and 0.0113, respectively. The volume resistivity is approximately 2×10^{16} ohm-cm.

For some Glass Resin compositions the dielectric constant decreases sharply with increasing temperature. For example, at 100Kc the dissipation factors are 0.069 and 0.025 at 25°C. and 146°C., respectively. In addition, as the temperature is increased, the frequency dispersion of the dielectric constants and dissipation factors diminishes, except at very low frequencies. Low dispersion is a desirable characteristic not normally found at elevated temperatures. It appears that Glass Resins may be useful as flexible high temperature dielectrics.

THERMAL PROPERTIES OF GLASS RESINS

The linear coefficient of expansion of Glass Resins is in the range ot plastics. In the range 0-300°C. the value is 1300×10^{-7}. Although this is considerably higher than most commercial glasses, resin to glass seals do not fail due to differences in coefficients of expansion because of the flexibility of the resin in thin films. Glass Resin films have been applied to stainless steel panels and cycled between —65°C. and +125°C. without loss of adhesion or resin failure. Furthermore, the coated panel can be bent through 180 degrees without damage. There are numerous indications that the linear coefficient of expansion of Glass Resins can be reduced by variations in the final cure procedure. Ultimately it is believed that values less than 100×10^{-7} will be obtained.

The effect of high temperatures on Glass Resins depends on the thickness of the specimen. In samples up to one-sixteenth inch thick, no change is observed for fifteen minutes at 400°C. in air, and there is no damage for several days at 300°C. In vacuum or in inert atmospheres, Glass Resins appear to be stable indefinitely at 400°C. There is little evidence of chemical degradation when the resins fail thermally. The usual effect is the propagation of large conchoidal fractures, not unlike those observed in poorly annealed glass. A very considerable part of our research efforts at the present time is being devoted to the solution of this problem.

MECHANICAL PROPERTIES OF GLASS RESINS

The specific gravity of unfilled Glass Resins lies in the range 1.20-1.50 g/cc. Type 100 has a tensile strength of 2,600 psi, compressive strength of 18,000 psi, flexural strength of 5,300 psi, modulus of elasticity of 200,00 psi, and a Rockwell R hardness of 130.

One of the most interesting characteristics of the resins is the ease with which they can be shaped by conventional tools. High speed drills, lathes, and milling machines have been used without difficulty. Unlike many organic plastics, there is no tendency for the resin to soften or chip. Grinding and polishing operations are extremely simple and effective.

CHEMICAL PROPERTIES OF GLASS RESINS

When completely cured, Glass Resins are non-flammable chemically inert materials. They will not dissolve in any of the usual organic solvents. Oxidizing and reducing agents are without effect except under the most extreme conditions. They are unaffected by water. Concentrated solutions of alkali and hydrofluoric acid slowly decompose the resins.

In the liquid form, Glass Resins are soluble in low molecular weight polar organic solvents, such as methanol, ethanol, acetone, and methyl ethyl ketone. It is also possible to interupt the final cure and obtain a thermoplastic solid which is soluble in these reagents.

RADIATION RESISTANCE OF GLASS RESINS

The radiation resistance of Glass Resins is exceptional. Type 100 resin was exposed for 500 hours to ultraviolet radiation without any visible effect. Similar samples were exposed to 920,000 rads of gamma radiation from a Cobalt-60 source, and to 5,000,000 rads of gamma and beta radiation from an enriched Uranium source with only slight pink coloration resulting. There was essentially no loss in transparency. Under the same conditions, ordinary glass is deeply and permanently discolored.

MISCELLANEOUS PROPERTIES OF GLASS RESINS

Liquid and vapor permeation studies on Glass Resins are still incomplete, although other indications show that they are good barrier materials. The out-gassing characteristics of the cured resins are good. Coated glass specimens have maintained static pressures of less than 10^{-6} mm Hg for weeks, even under electron bombardment. Vacuum tight seals are easily made between glass members. They have withstood two hours of steam autoclaving at 140°C. without cracking or loss of adhesion. Similar results are obtained with Glass Resin-coated metal panels.

HANDLING PROCEDURES

Glass Resins are supplied in solvents containing approximately fifty percent solids. These solutions have a shelf life of at least six months. The manner in which they are treated depends on the ultimate application desired. In any event, it is always necessary to first pre-cure the resin.

The pre-cure procedure removes the solvent and advances the polymerization to the maximum point at which the material is still workable. The procedure is extremely simple. The resin is transferred to a beaker and stirred slowly while heating on a hot plate or in an electric heating mantle. For Type 100, the maximum recommended resin temperature is 140°C. At this point the pre-cured resin is a clear liquid with a viscosity similar to that of glycerol at room temperature. It is important to complete the pre-cure as rapidly as possible since the final stage of polymerization is a function of both time and temperature.

If coatings, sizes or laminating applications are desired, the pre-cured resin is cooled to approximately 100°C. and dissolved in rapidly stirred chemically pure acetone. A five percent by weight solution will give a coating approximately one mil thick. The Glass Resin solution may be applied to the object to be coated by dipping, spraying, or brushing. Once this is done, the coating should be dried to a tack-free film at a temperature not exceeding 50°C. This usually does not take more than a few minutes. The final cure is affected by heating the coated object in an oven at 85-95°C. for at least 24 hours. The exact length of time depends on the thickness of the coating. As a general rule, about 24 hours should be allowed for each ⅛ inch thickness, up to ½ inch specimens. In other words, four days at 85-90°C. is sufficient time for any sample regardless of thickness. On thick specimens it is sometimes desirable to allow an additional one day post cure treatment at 120°C.

Either one of two procedures may be followed if Glass Resins are to be used as adhesives. When very thin bonding layers are desired, the acetone solutions described above may be used. Each member to be joined is covered with the solution, and the coating allowed to dry to a tack-free film. The two pieces are then held together under slight pressure while under-going the final cure in the oven at 85-95°C. A second procedure is to place the 140°C. pre-cured resin directly in the oven set for this temperature range. After several hours the resin will become a very tacky material which becomes a dry thermoplastic solid when cooled to room temperature. In this state the resin will flow readily between the objects to be joined, provided they have been heated to at least 100°C. The same final cure already described completes the process.

The solid thermoplastic Glass Resins have several interesting properties. There are indications that with appropriate fillers they can be compression molded. Even the unfilled resins will yield under the slow application of pressure, and maintain their conformations when the pressure is removed. These materials can be powdered and stored for long periods of time prior to use. The powders can also be used as adhesives, since they will flow with the application of heat and pressure.

When solid castings are desired, the 140°C. pre-cured Glass Resin is poured directly into the pre-heated mold, which is then transferred immediately to the oven for final cure. If possible, the mold should be lined with aluminum foil to facilitate removal of the cured casting. An alternative procedure is to coat the mold with a silicone release agent. Usually the casting can be removed from the mold after 24 hours. It should then be returned to the oven for completion of the final cure. Final shaping can be done by simple machining, grinding, and polishing operations.

CONCLUSION

An attempt has been made in this paper to describe the general properties and uses of a new family of inorganic polymers called Glass Resins. By changing the resin composition and incorporating fillers, the properties and the uses can be varied widely. It should be emphasized that Glass Resins are still experimental materials, and much is still to be learned about their chemical and physical characteristics. Owens-Illinois is expending an increasing amount of its research effort to this end. Both liquid and solid samples of Glass Resins are available to interested persons.

MANUFACTURE OF A GLASS THERMOMETER

FERDINAND M. WEISS
Accuracy Scientific Instrument Co.
Philadelphia, Pa.

INTRODUCTION

You are about to explore a world which is relatively unknown to most people. Encompassed in this world is the simplicity in theory and the detail in production. Starting with the raw materials and ending with a completed thermometer, we will explain how and why each step is necessary. Now, I would like to invite you to join me into this world of thermometers.

SELECTION OF TUBING

The first thing we must do, is to contact the Corning Glass Works where most of the thermometer tubing is made and choose the type of thermometer tubing which we need. We select this tubing by both composition and design.

As for composition, we may select a tubing which is similar to Corning #0010, and is called lead or soft glass. This is the most widely used tubing because of its lower cost and easy working characteristics. It may be used up to a range of 400°C. This glass softens at 648°C. and has an annealing point of 480°C. For ranges over 400°C. and up to 650°C., most manufacturers use a borosilicate tubing similar to Corning #7720. This tubing softens at 747°C. and has an annealing point of 600°C. Our company uses the borosilicate tubing only up to a temperature of 500°C. We then use an ignition tubing for temperatures up to 650°C. as we have found this tubing to be more stable at the higher temperatures but it is extremely hard to work with and is very expensive. Ignition tubing #1720, softens at 915°C. and has an annealing point of 715°C. For our purpose today, we will select the lead or soft glass.

Next comes the design of the tubing. As shown in Figure #1, there are five most common designs used in industries and laboratories today. "A" and "B" are similar in that they are both spirit bore tubing. As you can see, the bores or capillaries (the hole which runs up the center of the tube) are round and are used in thermometers which are to be filled with an organic liquid, usually red in color. These tubes do differ in outer shape. "A" is a lens tubing which magnifies the bore by its triangular shape, when one looks directly at its front. "B" has a round outer shape and is the more common of the two.

The other tubes "C", "D", and "E" are used in the manufacture of mercury filled thermometers. "C" is a lens tubing which differs from "A" only in the aspect that the bore is designed for mercury and not red liquid. "D" is called mercury oval bore tubing, having a round outer shape and an oval bore. It is the most widely used today, because of its easier workability. The oval shape of the bore enables the indicating media to spread over a wider area, making it easier to see. Last, but by no means least, is "E". This is the tubing which is most widely used by our company, the ACCURACY SCIENTIFIC INSTRUMENT COMPANY, and is known as

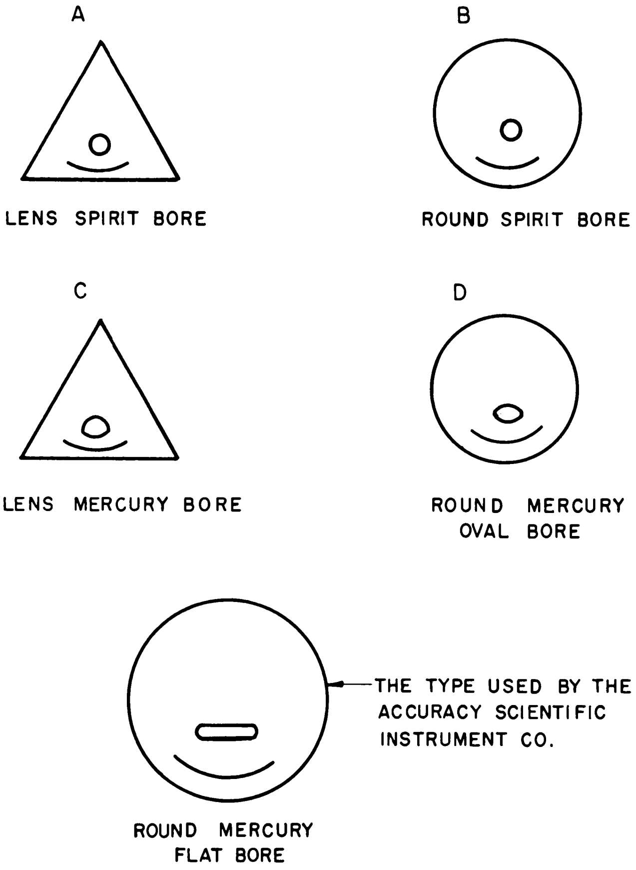


Figure I
Types of Tubing

"Flat-Bore" tubing. The outer shape is round, as is that of "D", but the vast difference is that this tubing has a flat, rather than oval bore. With a flat bore, as in Figure "E", the volume of the bore is spread over such a wide area that its cross sectional area looks like that of a book. As a result, the mercury column, in many instances, look two, three, and even four times wider than that of an oval bore. This, of course, is a great advantage to the user, but makes manufacturing much more difficult. As you can see in Figure "E", the walls of the bore are very close together and the edges become fairly sharp. With this design, the mercury has a tendency to cling to the glass instead of rising and falling smoothly, and can be corrected only by extreme care in manufacturing.

Since the use of the flat bore tubing involves such enormous care and tremendous detail in manufacturing, we will choose the easier working mercury oval bore tubing in Figure "D" for today, and go on with the next step.

Finally we must decide on either a white or yellow enamel backed tubing. Both are available in all of the designs we have explored with the white back tubing being the least expensive. However, with yellow back tubing, a thermometer is much easier to read because of the greater contrast between the silver mercury and the yellow color.

Along with the tubing for the stem portion, we must select tubing for the bulb of the thermometer. Corning Normal tubing #7500 or glass having similar properties is usually used. The softening point of this tubing is 702°C., and the annealing point is 536°C. It is most essential that the wall of the bulb glass be of the proper weight, not too thick or too thin. A thin wall tubing is more difficult to handle and will break easily. With a thick wall tubing, the instrument is less sensitive since any change of temperature will have difficulty in penetrating the glass to reach the mercury.

Now that we have selected the necessary tubings, we can proceed to fabricate a thermometer.

CALCULATING GOOD RESULTS

In order to obtain a good finished product, certain calculations must enable us to answer two questions. First, what bore size should be used and second, what bulb size?

In the thermometer industry, each company has their own system for determining these results. These systems have been set up by years of trial and error methods which have resulted in obtaining master tubes from which measurements of mercury volumes are made. These tubes are then used to determine the different bore and bulb sizes.

All our calculations are based on one simple fact. That different combinations of the bore and bulb sizes will give different distances that the mercury level in the bore will move per degree of temperature change. Therefore you may change this distance by two methods. One is to change the bulb volume, the other is to change the bore size.

Figure #2 shows the use of the first method. In Figure #2A, we have a finished thermometer. This instrument has a scale length of "L" millimeters. In Figure #2B, we take the same thermometer, make the bulb larger which in turn gives us a longer scale "J". In Figure #2C, we make the bulb smaller which in turn gives us a smaller scale "K".

To demonstrate the second method we use Figure #3. In Figure #3A we once again take a finished thermometer which has a scale length of "L". Now by using a smaller bore, we can obtain a longer scale "J" as in Figure #3B. Then by using a larger bore, as in Figure #3C, we get a smaller scale length "K".

Care must be taken when choosing a bore size so that it does not get too large or too small. When a bore gets smaller than .075mm, it becomes very hard to see unless it is flat in shape. In most cases, when a bore becomes larger than .2mm in a mercury bore and larger than .55mm in a spirit bore, you would have to seal on such a large bulb that it becomes impractical to manufacture.

Thermometers having large bulbs and large bores have one big advantage in that they are easier to read, but the instrument would have

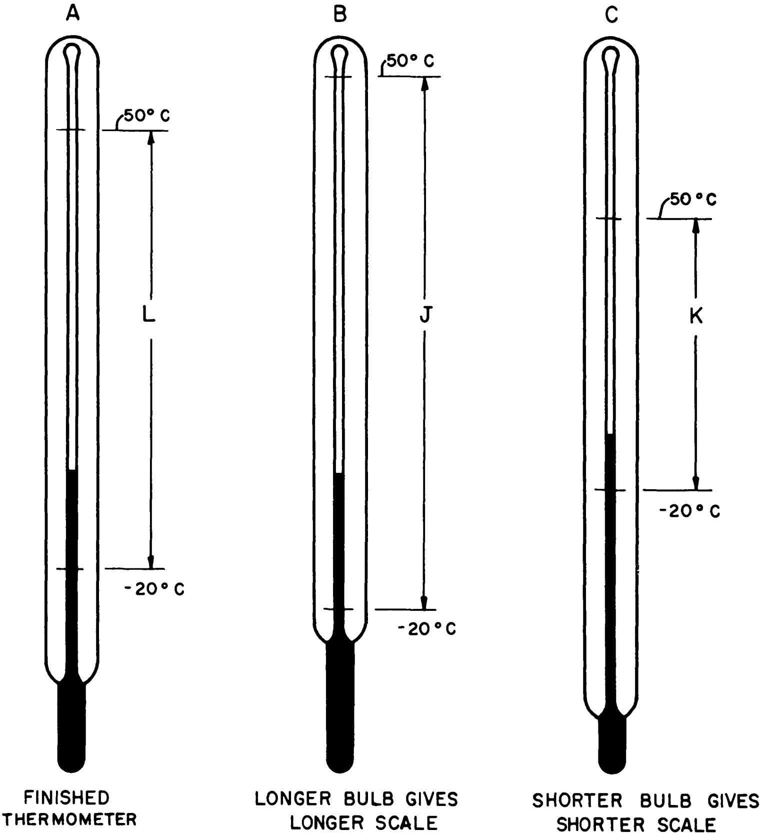


Figure 2
Change Bulb Volume

to be extremely large. With a small bulb and a small bore you can obtain the same results in a smaller package but it will be more difficult to read. A combination of a large bulb and a small bore will produce a very sensitive instrument.

THERMOMETER IN PRODUCTION

Before starting production of a thermometer, we must determine what is needed. Our thermometer will require a range of —20 to +50°C., with an oval-bore mercury filled tubing, 12″ in length. With these specifications in mind, we must select the proper tubing, having a bore size that will give us a bulb of a practical size.

The capillary tube as we first find it, will be cut to length with the ends square as in Figure #4A. To prepare the stem to receive the bulb we must heat one end of the stem in the conventional crossfire, closing the capillary and blowing a bubble or enlargement in the end of the stem. We then cut off the thin part of the bubble and as a result we have a funnel shaped enlargement in one end of the stem as in Figure #4B. This permits us to seal the bulb to the stem without closing the bore (Figure #4C). The seal can then be made with the aid of a crossfire, either by a lathe or manually.

Now we must close the bulb at the proper place in order to have the correct volume of mercury in it. This is determined by measuring specific amounts of mercury required to give us the correct scale length, when combined with the bore we have selected. This measured amount of mercury is placed in the bulb and a small mark made on the glass at the top of the mercury level as in Figure #4D. The mercury is then poured out and the bulb is closed (Figure #4E) at the mark by means of a pin fire.

At this point I think we should discuss the annealing processes. Basically all good grades of thermometers are annealed, some more thoroughly than others, depending on their use and design. The strain

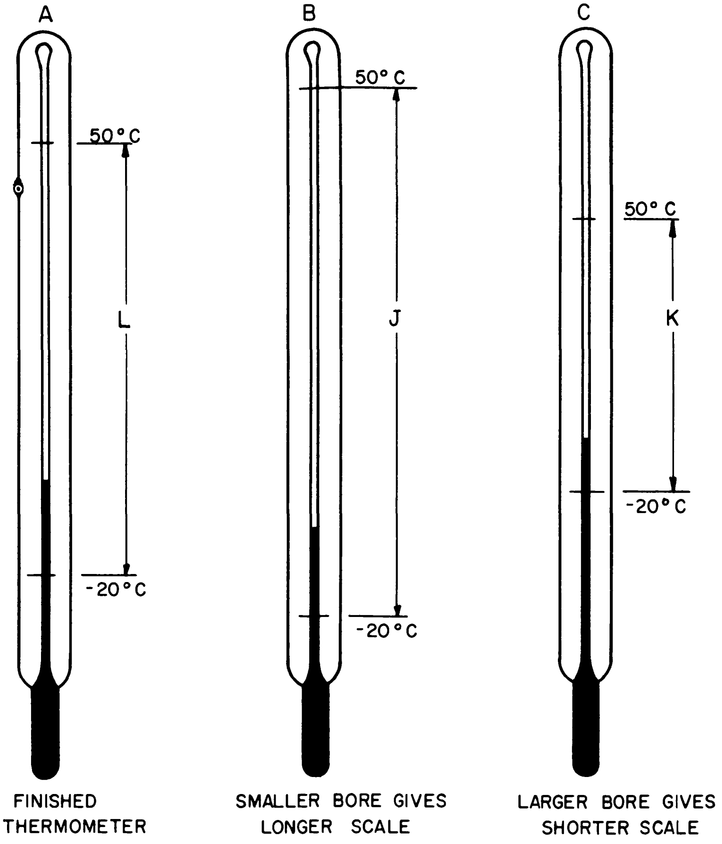


Figure 3
Change Bore Size

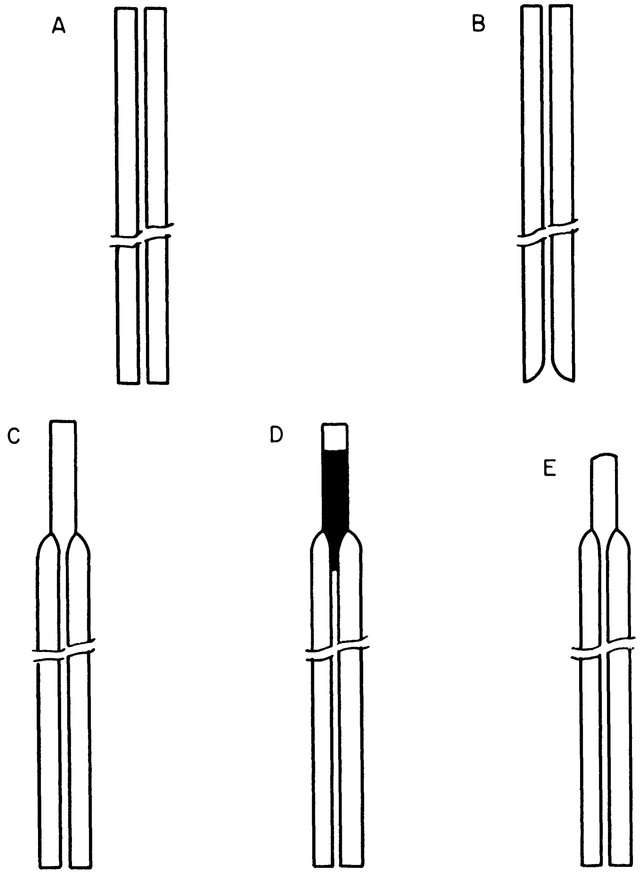


Figure 4
Glassblowing Steps

should be completely relieved from the bulb of high temperature instruments or those having fractional subdivisions such as 1/10°, 1/5° etc. This is necessary in order to obtain reproducible readings. To anneal an instrument, it is placed in an annealing oven and held at annealing temperatures for quite some time, then allowed to cool slowly thereby relieving the strain completely.

To fill the thermometer with mercury, which is the next step, the entire instrument is heated, thereby expanding the air in the instrument and driving out any moisture which is present. The thermometer is then inverted with the open end in a dish of mercury as in Figure #5. This process may have to be repeated several times until the thermometer is completely filled.

With modern production systems, thermometers are filled by putting several hundred instruments into a vessel at one time. The vessel is then heated and a vacuum is pulled. Mercury is then introduced into the vessel and the vacuum is released, in turn, filling the thermometers.

Other indicating media can be used depending on the particular design of the instrument. For example, on a low temperature mercury thermometer, it is necessary to use mercury-thallium. This amalgam of mercury and thallium has a freezing point of about —55°C., compared to —40°C., with plain mercury. Extreme care must be taken when working with this amalgam for it must be used and stored under a vacuum or under an atmosphere of nitrogen because it oxidizes immediately when exposed to air. This amalgam is preferred at low temperatures because it is a more accurate medium than the organic liquid.

Then there are also the spirit or red liquid filled thermometers. Instruments containing organic liquid fillings are filled under a vacuum with the absence of heat. Organic liquids would ignite if heat were applied during the filling process. The chart in Figure #6 describes the common types of liquids used and under what circumstances.

After we have finished the filling process, we have an instrument which is completely filled with mercury as in Figure #7A.

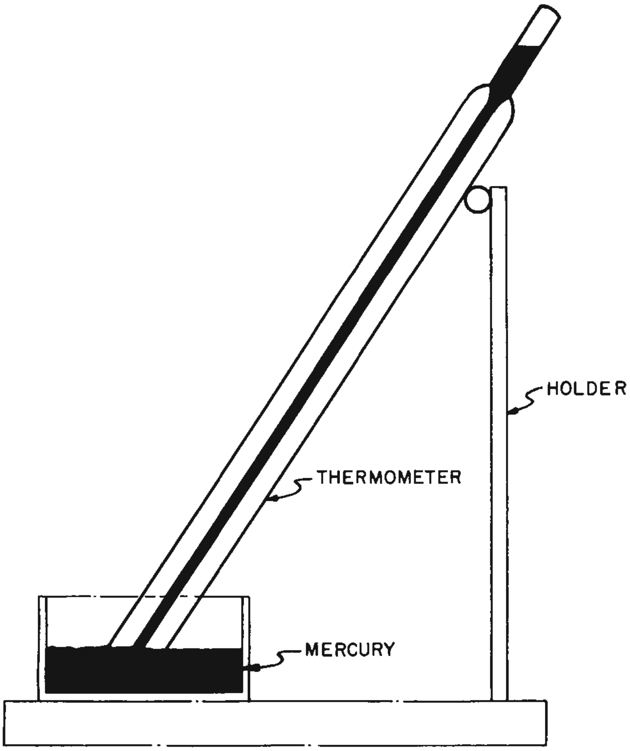


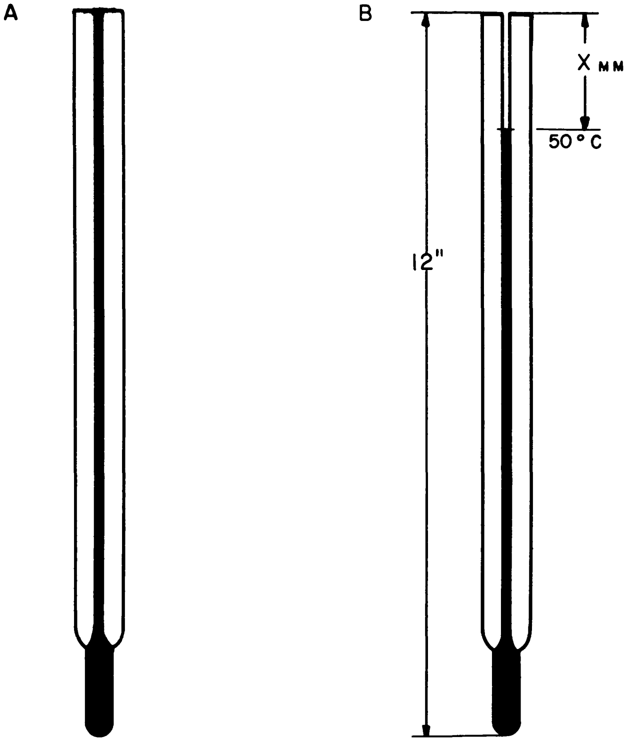
Figure 5
Filling Thermometer

All liquids are clear and a red pigment is added to them.

NAME OF LIQUID	TEMPERATURE RANGES USED AT
Pentane	-200 C to +20 C
Pure Alcohol	-100 C to +20 C
Toluol	-80 C to +50 C
Xylene	-40 C to +92 C
Crimsoline	-18 C to +150 C

Figure 6
Organic Liquids

Our next step is to remove some of the mercury so that we will have a mercury level between the temperatures of —20 to +50°C., as previously determined. Figure #7B illustrates this procedure. The first thing we do is cut the instrument off at its exact length (12″). We do know



THERMOMETER COMPLETELY FILLED WITH MERCURY

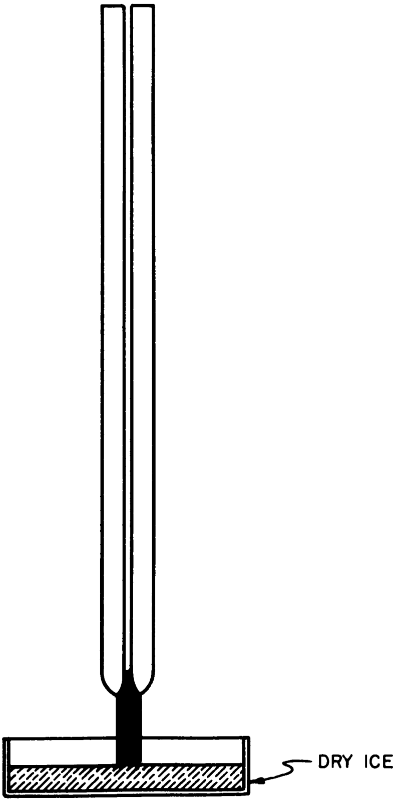
THERMOMETER AFTER EXCESS MERCURY IS REMOVED

Figure 7
Removal of Excess Mercury

that when the instrument is subjected to a temperature of 50°C., the mercury column should be near the top of the thermometer. For our purpose we will call the distance "X" millimeters from the top. The bulb end of the thermometer is immersed into a water bath that has been heated to a temperature which will cause the excess mercury in the instrument to overflow. This temperature will always be higher than the maximum range of the instrument, which in our case is +50°C. After this process the thermometer has just enough mercury in it so that the mercury level will be "X" millimeters from the top when subjected to a temperature of +50°C.

There are other methods used to obtain the right amount of mercury but we will not go into them at this time since we have described the most widely used method.

The next step is to fill the thermometer with nitrogen. This is done by putting the instrument into an atmosphere of nitrogen and immersing



DRAW MERCURY LEVEL
INTO BULB

Figure 8

Pressurize Instrument

the bulb in dry ice. Then the mercury level is drawn into the top of the bulb as in Figure #8. By means of a crossfire, the top of the thermometer is heated and the instrument finished off with a round or ring top. The bulb was kept cold to make sure that the mercury column remained in the bulb until we had almost completely finished the instrument. Then just before the heated top had a chance to cool, we allowed the mercury to rise, creating a pressure against the top of the bore causing it to enlarge resulting in an expansion chamber. The expansion chamber is needed for basically two reasons. The first is so that we may run the mercury up into the chamber to reunite the mercury column which may become separated in shipment. The second is so that if the instrument is subjected to a temperature, higher than its maximum range, the mercury will flow into the chamber, preventing breakage. On most low range thermometers, the chamber is made large enough to accommodate a temperature of 100°C., unless stated otherwise.

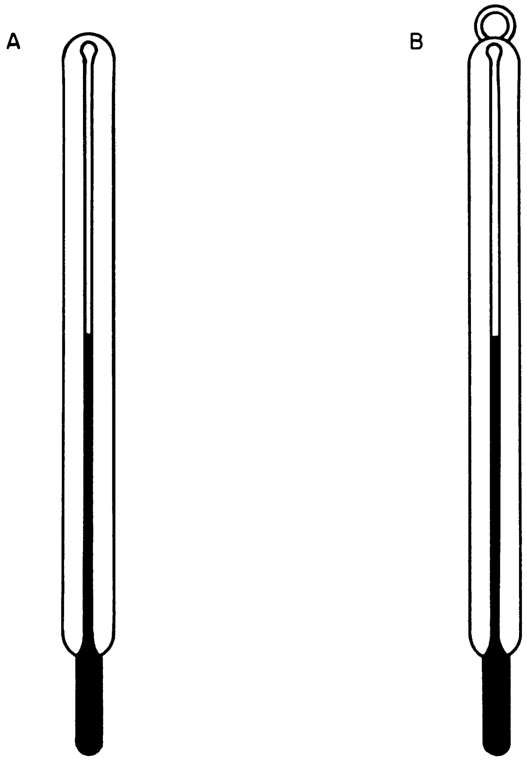
Now why did we go through the process with the nitrogen? Well, we draw the mercury column down into the bulb so that after the thermometer was finished, there would be a pressure above the mercury column. This pressure would be in the form of a gas, which is nitrogen. Nitrogen is used so that there will be no moisture or impurities in the gas that may contaminate the mercury and cause it to cling to the sides of the bore. The nitrogen is very important especially if we had used the FLAT-BORE which is used by the ACCURACY SCIENTIFIC INSTRUMENT CO. With the flat bore, care must be taken to see that no air is allowed to enter the instrument. If it does, the thermometer becomes practically inoperative. However, in an oval bore instrument, some air may enter the instrument without causing any harm. Figure #9 illustrates the completed unengraved instrument.

The final step in this stage of production is the inspection of the completed blank to see that the mercury rises and falls freely and that there are no gas pockets below the mercury level either in the bore or the bulb.

CALIBRATION AND ENGRAVING

To calibrate the thermometer we have selected, with a range of —20 to +50°C., we will need only water and alcohol baths. In calibrating other instruments with different ranges, we might use oils of varying weights and possibly a salt bath for very high temperatures. We first put our thermometer into the appropriate bath solution along with a thermometer which has been certified by the National Bureau of Standards. The bath is then heated to the temperature at which we would like to calibrate the instruments. When the N.B.S. thermometer reaches that temperature, we place a small mark at that mercury level on the instrument we are calibrating. A thermometer may be calibrated at innumerable points depending on the length of the scale and the accuracy required. A longer scale length usually requires more points although no matter how short the scale is, the instrument should always be calibrated at not less than two points.

The instruments are now ready to be engraved. The engraving process is similar to that used on other types of volumetric glassware. They are



THERMOMETER FINISHED
WITH A ROUND TOP

THERMOMETER FINISHED
WITH A RING TOP

Figure 9
Completed Unengraved Thermometer

wax coated, the lines and numbers are cut through the wax and then etched with Hydrofluoric Acid.

CONCLUSION

We have just gone through the process of manufacturing a mercury-in-glass thermometer. From the ordering of the tubing through each step in the glassblowing process and touching lightly on the calibration and engraving methods.

We now have a completed instrument that we may view with a certain amount of pride. For we did not put the glass into a machine, push several buttons and come up with a thermometer. Instead, we performed each calculation, seal and calibration by using our minds and our hands. We started with little and ended with an instrument that plays an important part in obtaining success, whether it be in industry, research, education or any other field of endeavor. What is it?

A THERMOMETER.

THE "SPECIAL GLASS" TREND

F. L. Bishop
Technical Advisor for
Consumer and Technical Products Division
Owens-Illinois Glass Company
Toledo, Ohio

Read by
Robert Miller
Owens-Illinois Glass Co.

Those of us who have worked with glass for a good many years are frequently amazed at the accelerating pace of research and development in new glass compositions. This is, of course, the trend in all technologies, and we are fortunate to work in one of the few ancient technologies which is taking part in all the newer scientific triumphs of today and tomorrow. Glass takes part in space craft, lasers, computers, fiber optics, nuclear energy control and many other of the complications of modern science.

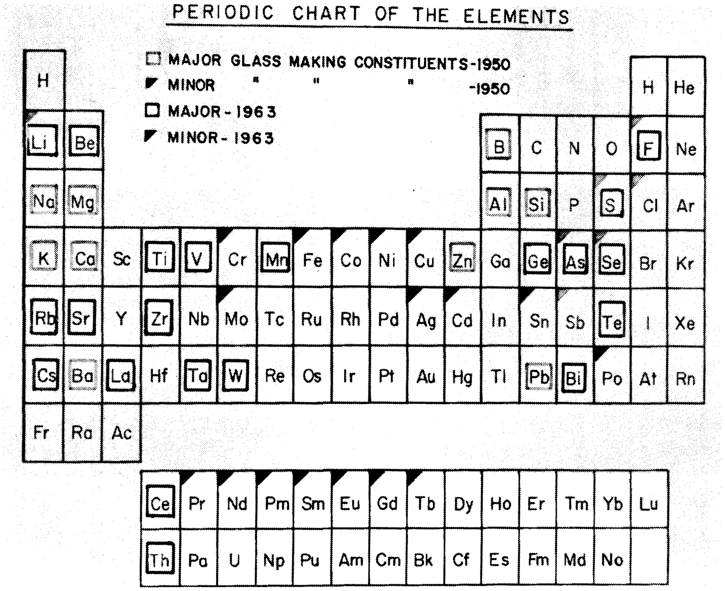


Figure I
Periodic Chart of the Elements

Figure 1 shows one form of the periodic table of the chemical elements. On this I have indicated in green the elements used in glasses which Kimble made only a few years ago, and in red the added elements we used in commercial glasses during the last year. I'm not sure the list is complete, but it is startling nevertheless. As Scientific Glassblowers you have long considered KG-33 as a "hard glass" and KG-12 as a "soft" glass. On Figure 2 I have illustrated this range of glasses by plotting softening points and annealing points against temperature. The lines drawn between are merely to connect the points for each glass and do not follow the actual glass viscosity change. On the right are the same points for the glasses we offer today.

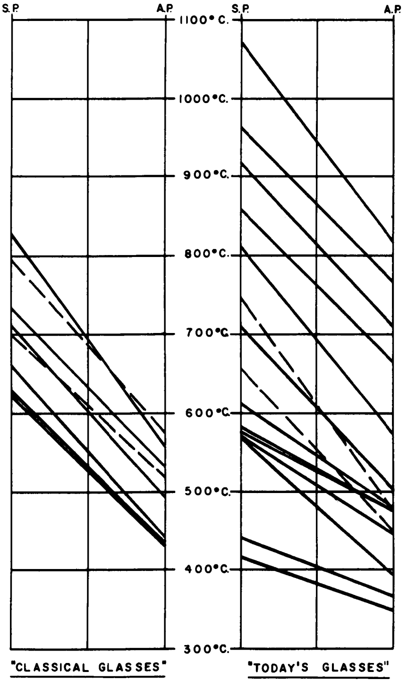


Figure 2

Comparative Range of Glasses

Very hard glasses are required to withstand application temperatures for special coatings, for vacuum use where high temperature bakeout is required or for high service temperatures. For substrates, the chief requirement is that the glass contain no elements that would gradually diffuse to the surface and poison the active material placed thereon. This generally means that the glasses must be free of alkalis and/or boron. The glass must not contain any elements which are easily reduced to metallic form such as lead or antimony, and obviously the glass must maintain its shape at the high temperatures used in applying the surface coating. Finally, the thermal expansion of the glass should match the material placed on it. No one glass is suitable for all substrate requirements, so a family of glasses has developed. Kimble technical people will be glad to recommend the best glass for each need. Fused silica is the classic hard glass for high vacuum work, but its permeability to helium and hydrogen makes other hard glasses more suitable in many instances.

Very soft glasses on the other hand are required when it is desirable to seal harder glasses, or glasses and metals without the necessity of reannealing the whole. Kimble solder glasses are available to cover a wide range of such uses. Soft glasses are used as lubricants in extrusion of metals or protecting metal surfaces from oxidation during other operations on metal ingots. The uses for encapsulating micro-circuits are well known and here again we must guard against elements that would poison the electronic parts and must make a hermetic seal at temperatures which their components can withstand. A final reason for making some very soft glasses is that certain properties, such as a high dielectric constant, are the result of adding elements to the glass which also make the glass soft.

During the past few years Committee F-1 of the A.S.T.M., which deals with materials for electron devices, has sought to standardize the metals used for glass sealing. The first of these specifications was issued in 1961. It bears the number F 16-61 T and specifies the properties to be maintained in the well-known iron-nickel-cobalt alloy which bears many trade names, such as Kovar, Therlo, Rodar, etc. The thermal expansion of this alloy is shown in Figure 3.

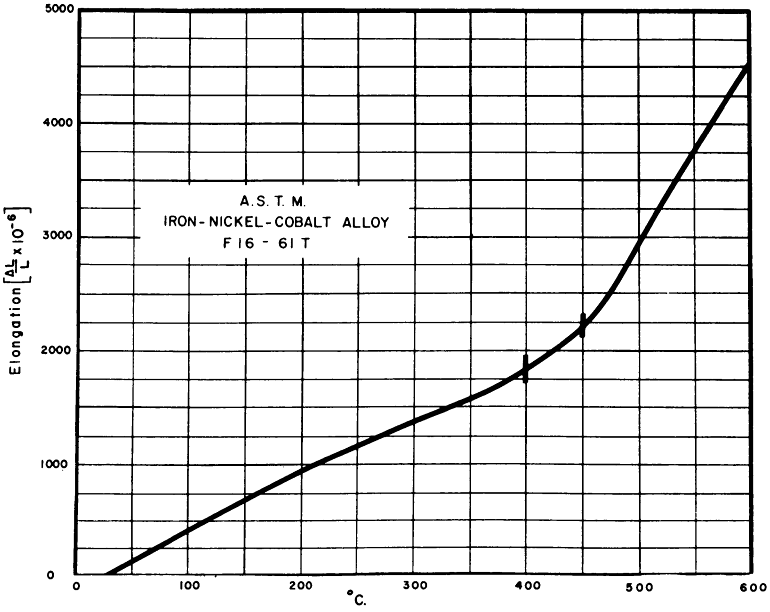


Figure 3

Expansion Curve, Iron-Nickel-Cobalt Alloy

It should be understood that the curve shown in Figure 3 has been listed "for information only", and the specification is limited to only two temperatures where the range allowed is shown by the red line. The next figure (Figure 4) shows the same metal, but with some thermal contraction curves of Kimble glasses added. These are the most commonly used glasses, several others are made for special purposes that will seal to this same alloy.

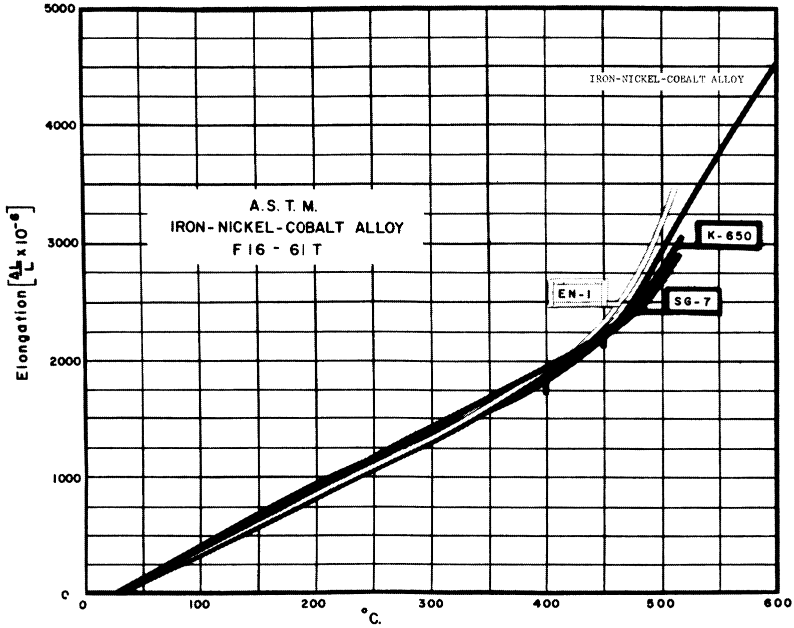


Figure 4
Expansion Curve, Iron-Nickel-Cobalt Alloy and Contraction Curves, Kimble Glasses

In 1963, the specification on iron-nickel sealing alloys, A.S.T.M. F 30-63T, was published. This covers four ranges of nickel content. Figure 5 shows the alloy #52, with its "information only" expansion curve, and the specification limits again in red. Figure 6 shows the same curve with appropriate Kimble glasses added. Figures 7 and 8 are for the #48 alloy, and Figures 9 and 10 for the #46 alloy. This #46 alloy is made chiefly for use with glazed ceramics. Figures 11 and 12 are for the last of the four nickel-iron alloys, #42.

Also in 1963, a specification for a 42% nickel-6% chromium-iron alloy, A.S.T.M. F31-63T, was issued. This alloy, commonly called #4 alloy, is shown as before on Figure 13, and with Kimble glasses, on Figure 14. A specification for chromium-iron alloys is in the works. The 18% chromium-iron alloy is shown in Figure 15, and again with appropriate Kimble glasses, in Figure 16; while the 28% chromium-iron alloy is the subject of Figures 17 and 18.

Other metals of interest today are tantalum and silicon. For tantalum sealing Kimble is announcing the availability of a new glass, IN-3. This is available in the form of tubing or in ground glass.

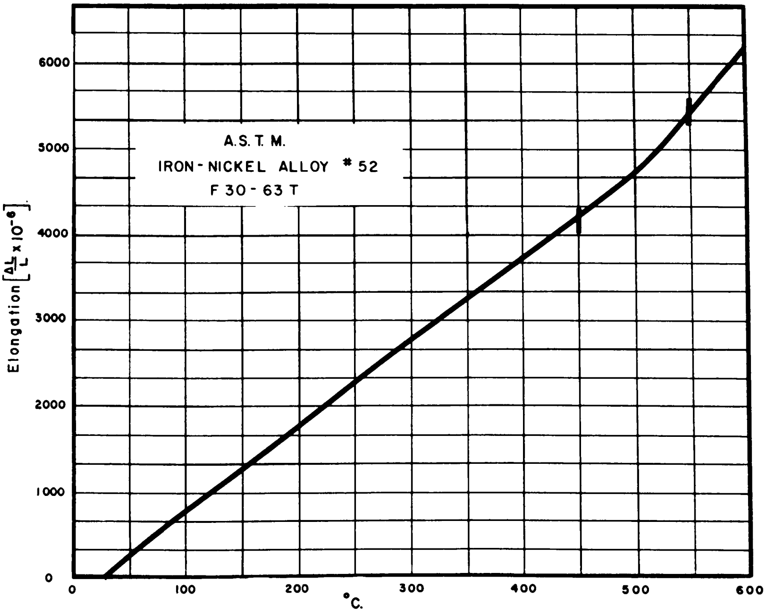


Figure 5
Expansion Curve, #52 Alloy

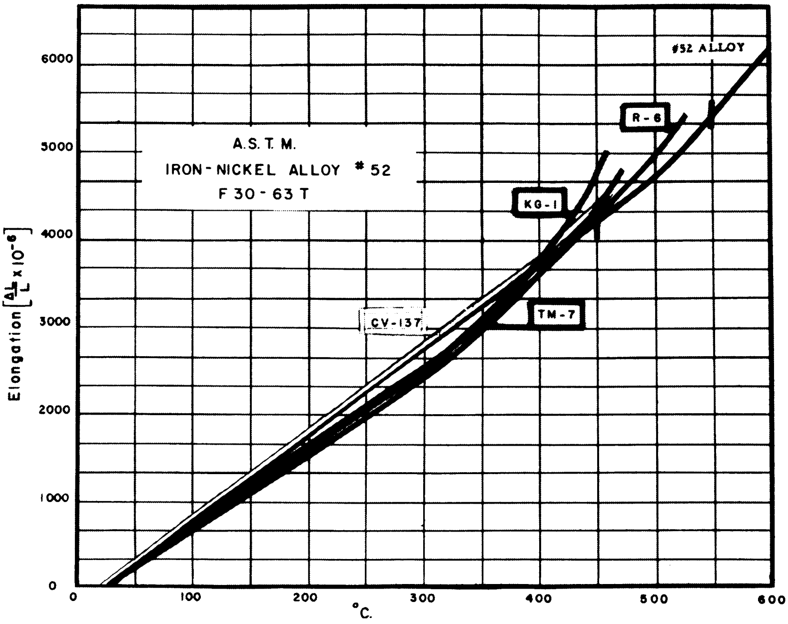


Figure 6
Expansion Curve, #52 Alloy and Thermal Contraction Curves, Kimble Glasses

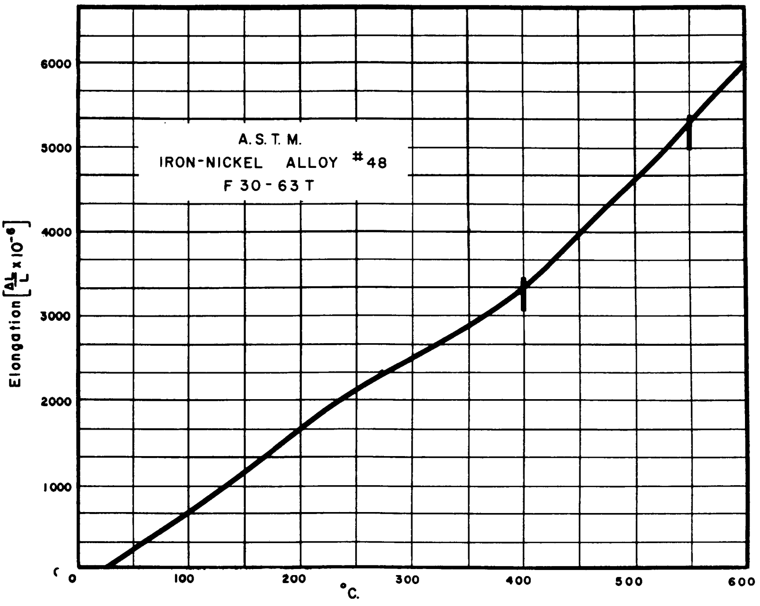


Figure 7
Expansion Curve, #48 Alloy

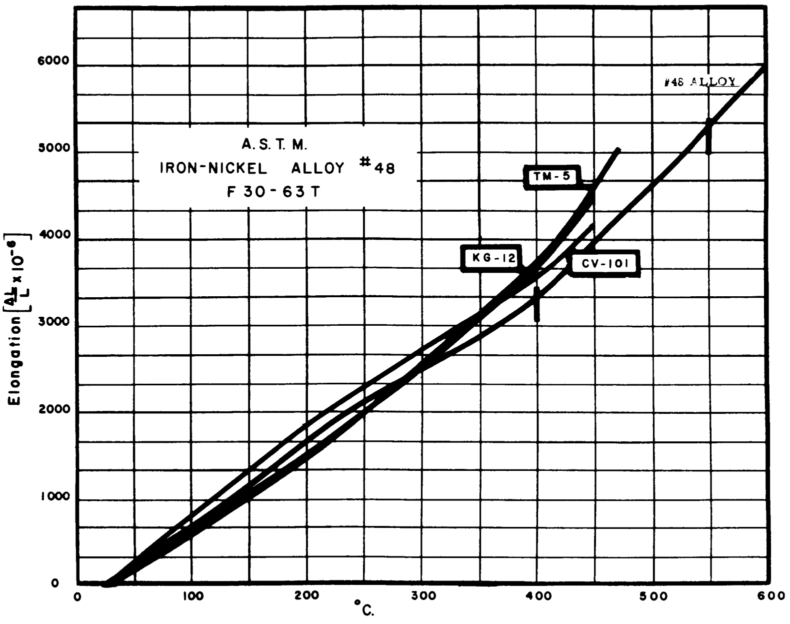


Figure 8
Expansion Curve, #48 Alloy and Thermal Contraction Curves, Kimble Glasses

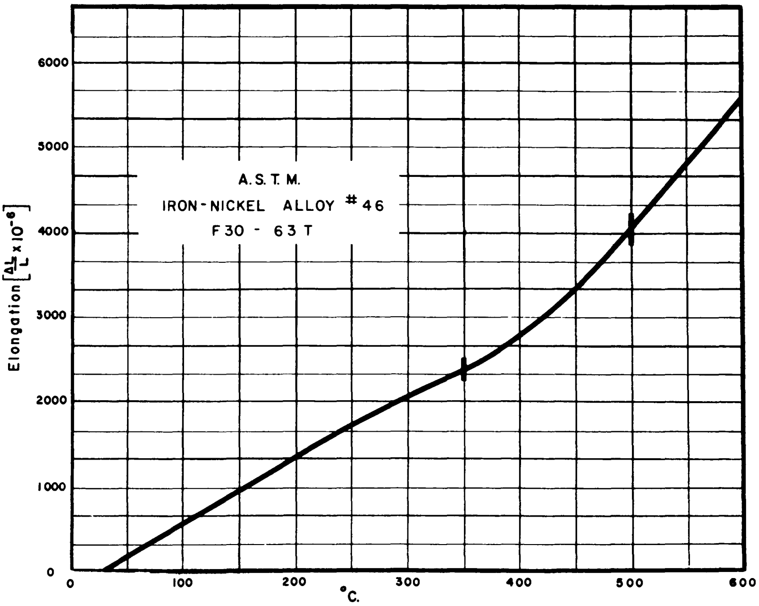


Figure 9
Expansion Curve, #46 Alloy

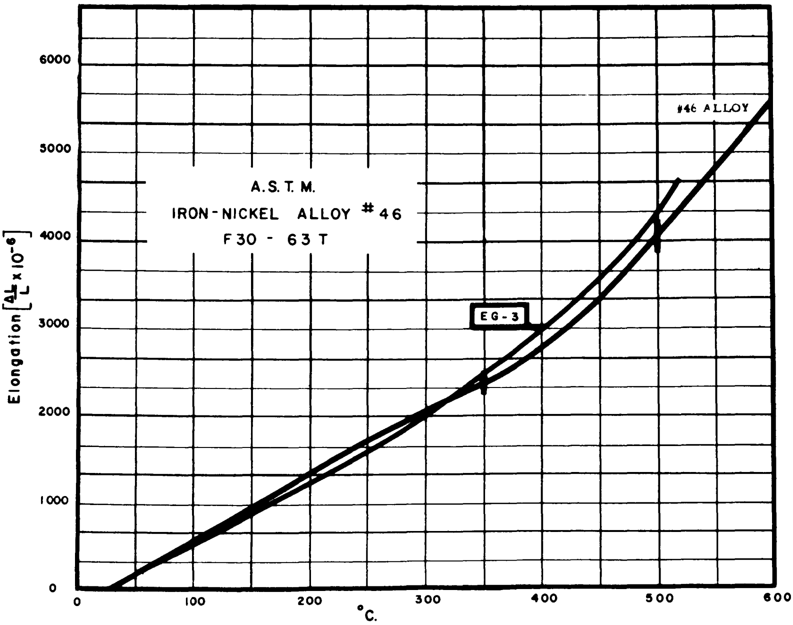


Figure 10
Expansion Curve, #46 Alloy and Thermal Contraction Curves, Kimble Glasses

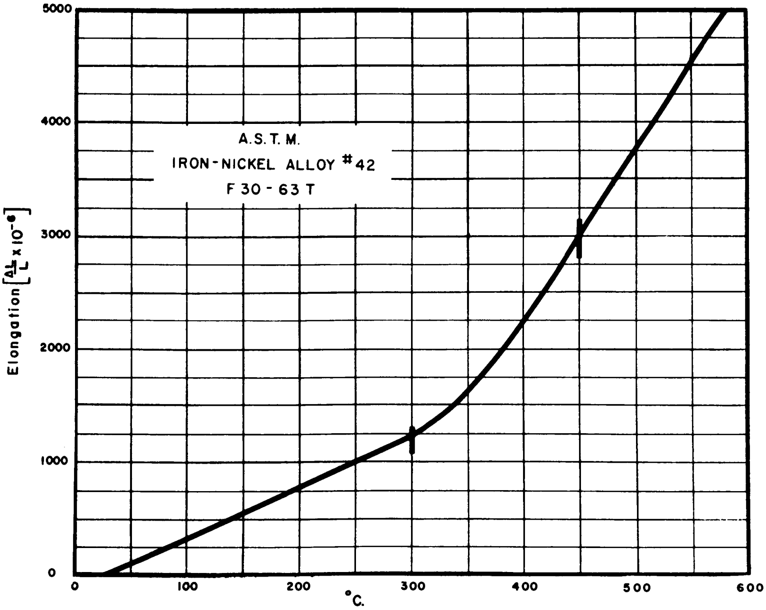


Figure 11
Expansion Curve, #42 Alloy

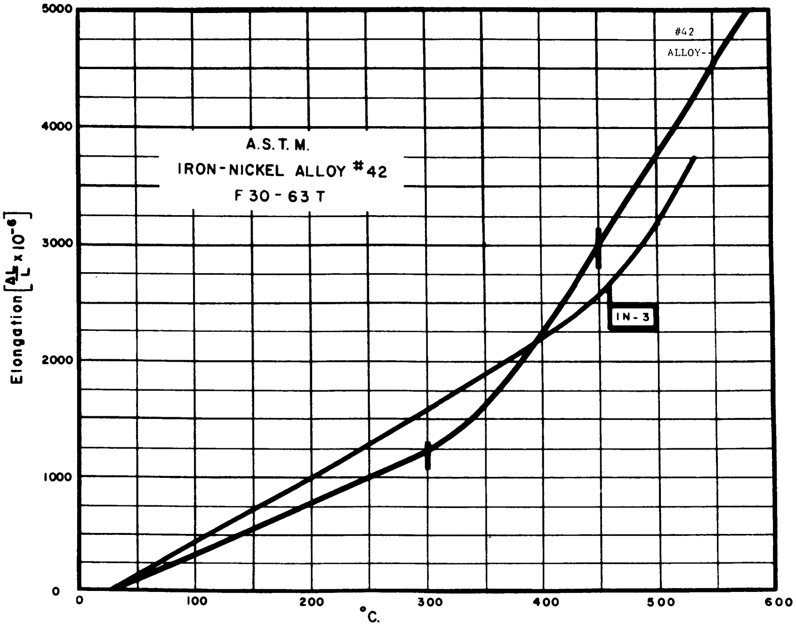


Figure 12
Expansion Curve, #42 Alloy and Thermal Contraction Curves, Kimble Glasses

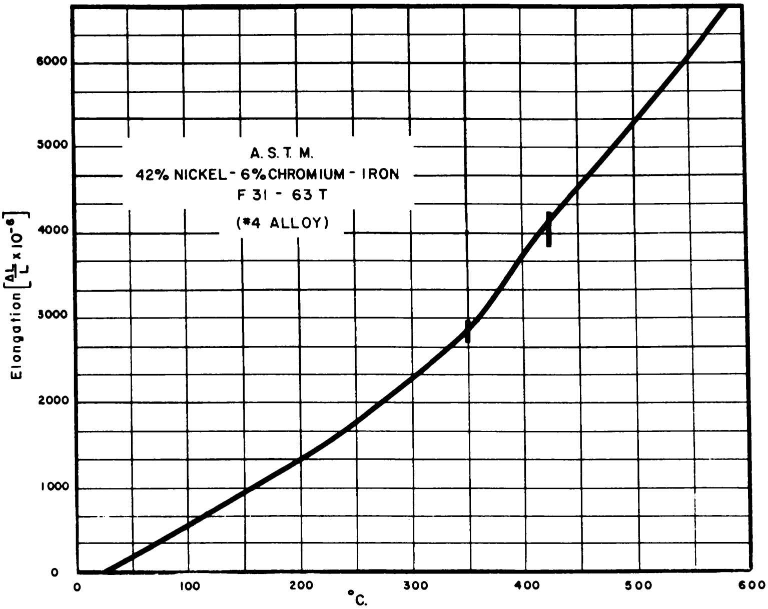


Figure 13
Expansion Curve, #4 Alloy (42% Nickel)

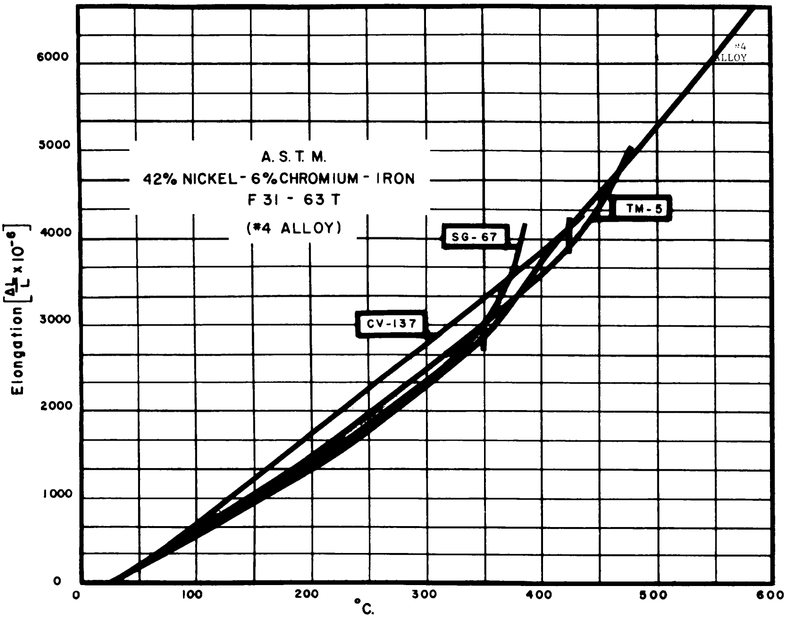


Figure 14
Expansion Curve, #4 Alloy (42% Nickel) and Thermal Contraction Curves, Kimble Glasses

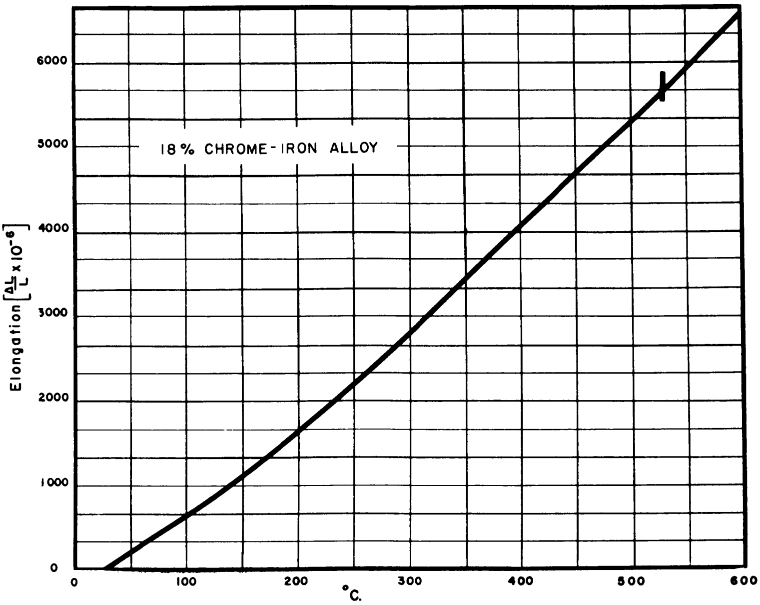


Figure 15
Expansion Curve, 18% Chromium-Iron Alloy

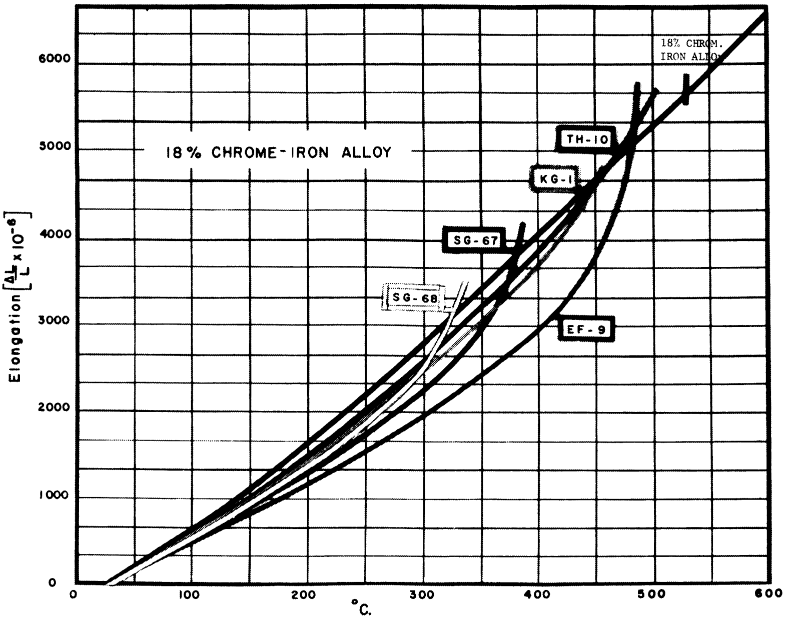


Figure 16
Expansion Curve, 18% Chromium-Iron Alloy and Thermal Contraction Curves, Kimble Glasses

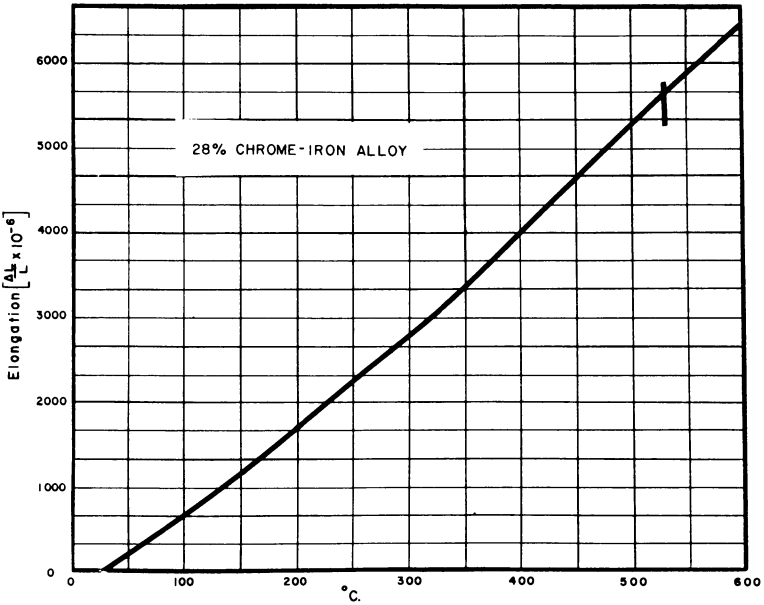


Figure 17
Expansion Curve, 28% Chromium-Iron Alloy

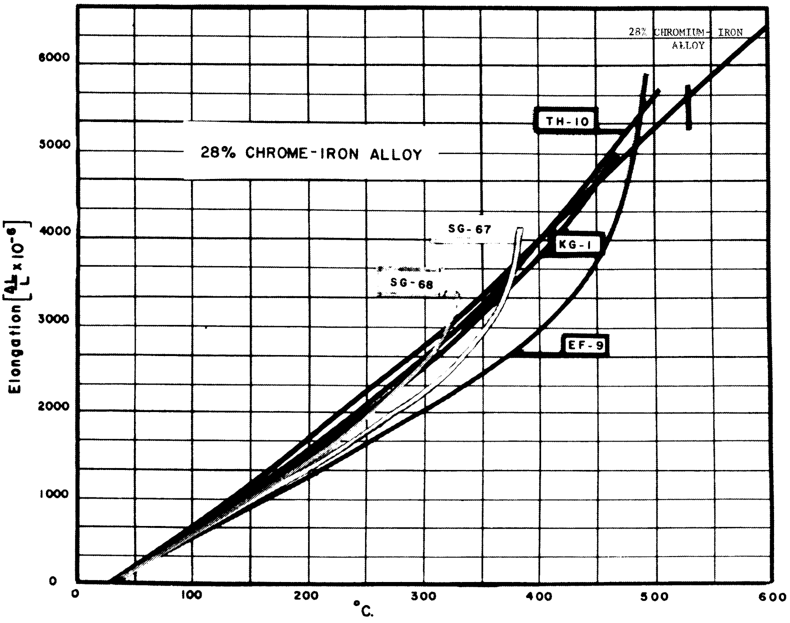


Figure 18
Expansion Curve, 28% Chromium-Iron Alloy and Thermal Contraction Curves, Kimble Glasses

For use with silicon we have the well-known KG-33, and in ground form only, EE-5, which has a softening point of 1070° Centigrade.

In addition to these requirements, the glassblower is frequently called upon to meet special chemical durability requirements which range from containing hot alkali vapors and caustic liquids to hydrofluoric acid. We suggest that when faced with such special problems you ask your Kimble sales representative or write or phone us in Toledo. The requirements vary too much to list the answers here.

Owens-Illinois is a supplier of glasses for fiber optics applications. In this field the new glass developments are frequent, and again we suggest an inquiry if you have special needs.

We are prepared to offer glasses for special applications having very high to very low electrical resistivity, dielectric constant, or dielectric loss, as well as glasses for transmitting or absorbing radiant energy or nuclear radiations.

We in Owens-Illinois do not intend to be left behind by the wave of new requirements in glasses. We cannot meet all the desired property requirements in glasses, but we will do all we can to help you, the glassblower, to satisfy your clients.

DESIGNING WITH GLASS AND TFE PLASTIC

JOSEPH F. McLAY
Labcrest Scientific Division
Fischer and Porter Company

INTRODUCTION:

The use of Tetrafluorethylene, hereinafter abbreviated TFE, has been found to have a number of unique properties that make it an extremely useful material in the design of scientific apparatus. Among the four major fluorcarbon plastics available to us today, TFE is the most widely used. This resin has a strongly bonded molecular structure consisting of only carbon and fluorine atoms, which results in a remarkable combination of chemical and physical properties. The only materials that seriously affect TFE plastic are chlorine trifluoride, oxygen difluoride, fluorine at high temperature, liquid fluorine at high velocity and molten alkali metals.[1]

Since there are so few materials that attack this plastic, it has gained wide acceptance for use in apparatus required by the scientific research community. The proper combination of TFE and glass materials of construction generally results in a product that heretofore was objectionable from a mechanical or chemical aspect. It should be of interest, therefore, to consider some of the major elastic properties of TFE, and to then discuss how several of these properties are used in finished products.

TFE fluorocarbon resins are engineering materials whose performance in any given application may be predicted by the theory of elasticity.

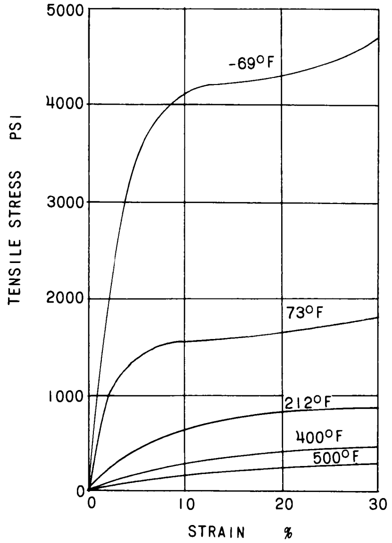


Figure I

STRESS VS STRAIN in tension to 30% strain.
Material—molded TFE
(Courtesy of Du Pont and Machine Design)

However, just as the properties of woods are different from those of metals, the properties of TFE resins are different from those of other engineering materials. From the following generalized data, strength, values can be selected which will allow the use of standard engineering design equations.

TENSILE STRESS:

Fig. 1 is a stress-strain curve under various temperature conditions, where the stress is in tension. Strain in this curve is expressed as a percentage change in dimension of the unstrained material. For instance, if a 1″ long TFE bar is stretched .100″, the percentage of strain is 10%, and the resulting internal tensile stress at 73°F. is 1600PSI. Fig. 1 shows that the stress-strain curve begins to deviate from linearity at strains of only a few percent. This is not the case for conventional glasses. Glass is perfectly elastic up to the point of fracture; that is, the stress-strain curve is linear.

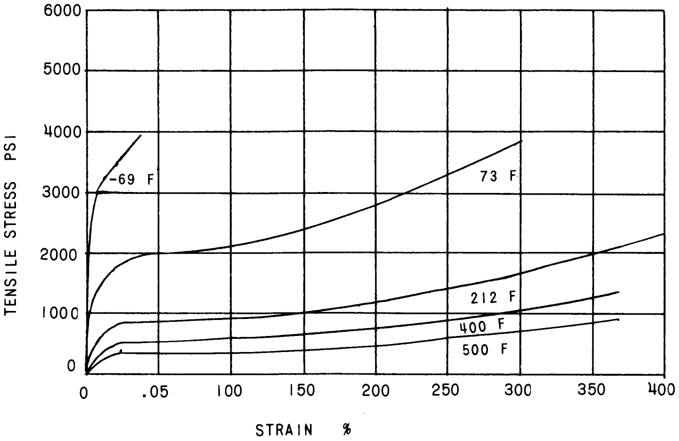


Figure 2

STRESS VS STRAIN in tension to fracture.
Material—molded TFE
(Courtesy of Du Pont and Machine Design)

Since TFE exhibits large deformations, it is usually advisable in design work to select an acceptable strain and then to determine the resultant stress from the proper curve. Fig. 2 gives the ultimate tensile strength, or the point of fracture, at various temperatures. The scale has been compressed relative to Fig. 1 in order to illustrate the entire strain scale.

COMPRESSIVE STRESS:

Stress-strain curves for TFE in compression are shown in Fig. 3 for three temperatures. The compression curves are similar to those in tension at low strain values; however, as the strain increases, the similarity ceases.

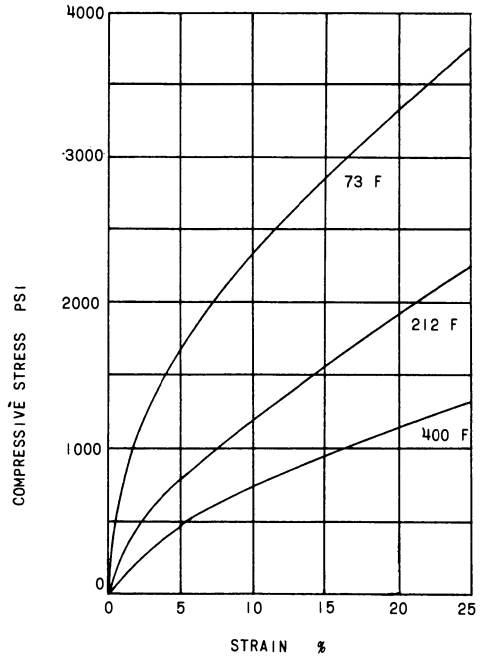


Figure 3

STRESS VS STRAIN in compression to 25% strain.
Material—molded TFE
(Courtesy Du Pont and Machine Design)

MODULUS OF ELASTICITY:

The ratio of stress to strain is defined as the modulus of elasticity.

$$E = \frac{s}{e}$$

Where E = modulus of elasticity, PSI
s = stress, PSI
e = unit strain, in/in

When designing for a given strain, the foregoing curves may be used to determine a value of E. For instance, a bar 1.5″ long is caused to elongate .060″ at 212°F. The value of $e = .040$ in/in, or 4%. Using the proper curve in Fig. 1 for a tensile strain of 4%, the corresponding value of tensile stress is 400 PSI. The tensile modulus of elasticity then becomes:

$$E = \frac{400}{.040} = 10{,}000 \text{ PSI}$$

It may be seen from this example and from the non-linear stress-strain curves that the elastic modulus of TFE depends heavily upon the temperature and allowable strain. Values for glass also depend to some degree on temperature, and for most glass compositions the elastic modulus decreases with increasing temperatures. Exceptions to this include silica glass and low-expansion borosilicate glasses where the modulus increases to a point with increasing temperatures. The elastic modulus for glass is independent of strain, providing the strain is selected below the point of fracture. The value for a typical low-expansion borosilicate glass at room temperature is 9.1×10^6 PSI, while the value at 930°F. is 9.5×10^6 PSI.[2]

POISSON'S RATIO:

From experimental results, it is observed that the extension of an element in the *x* direction is accompanied by lateral contractions in the *y* and *z* directions, and we have

$$e_y = e_z = -ve_x$$

in which v is a constant known as Poisson's ratio.[3] The value of Poisson's ratio for TFE is a function of temperature, and range from .46 at 73°F. to .36 at 212°F.

For most commercial glasses Poisson's ratio at room temperature is found to range between .20 and .25.

CREEP AND COLD FLOW:

A plastic material subjected to continuous loading undergoes a continued deformation with respect to time, and is known as creep. The deformation of most plastics is significant even at room temperature or below; thus the name "cold flow". Creep is the total deformation under stress after a specified time in a given environment beyond that instantaneous strain which occurs immediately upon loading. Independent variables which affect creep are time under load, temperature, and stress level.[4]

Creep is a consideration which must be investigated by the designer. Parts that are placed under continuous loads for long periods of time must be designed so that the part does not fail due to creep. The part under

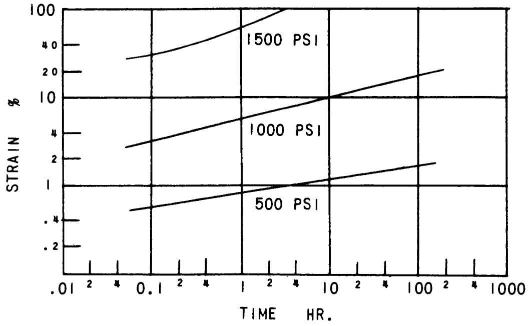


Figure 4

STRAIN VS TIME for tensile loading at 73°F.
Material—molded TFE
(Courtesy of Du Pont and Machine Design)

consideration might be an interface gasket for glass pipe, or the seal in a teflon needle valve. Fig. 4 illustrates how TFE resins at 73°F. continue to deform or cold flow following the initial strain. These curves are for tensile loads at three different stress levels. For all practical purposes, curves of deformation versus time eventually tend to level off; that is, the rate of change of strain with respect to time approaches zero.

Creep under load also occurs in glass, and is known as the elastic after-effect. When a load is applied to a glass specimen, the deflection will increase slightly with time following its application. After the load is removed, the glass will not completely recover its original form. Elastic after-effects in glass are relatively small, with the rate of movement decreasing rapidly and exponentially with time.

It has been found that soda-lime glasses have the highest elastic after-effect. For instance, after one minute of load removal, 2.2% of the original deformation still remains in the glass. Silica glass, on the other hand, has the lowest elastic after-effect with a value that is about 1/10 that of soda lime. The elastic after-effects of glass increase with temperature.[5]

APPARENT MODULUS OF ELASTICITY:

The apparent modulus is a convenient method of expressing creep in TFE. As long as the stress level is below the elastic limit of the material, the apparent modulus takes into account the initial strain plus the amount of strain that occurs with time.[4] Thus the apparent modulus E_a is

$$E_a = \frac{\text{Stress (PSI)}}{\text{Initial strain} + \text{creep}}$$

To illustrate, suppose from Fig. 1 it is determined that a part at 73° developed 500 PSI stress level due to a 1.5% strain. The modulus of elasticity is:

$$E = \frac{500}{.015} = 33{,}300 \text{ PSI}$$

If the part must sustain the load for 40 hours, the total deformation from Fig. 4 is 15%. Therefore:

$$E_a = \frac{500}{.15} = 3330 \text{ PSI}$$

For 100 hours of loading, the total deformation is about 18%.

$$E_a = \frac{500}{.18} = 2780 \text{ PSI}$$

It can be seen that creep tends to level off as time increases.

STRESS RELAXATION:

Stress relaxation is a phenomenon encountered when materials subject to creep are used in high tensile or compressive applications. The classic example is the TFE gasket used between two flanged sections of pipe. Under a continuous compressive force, the TFE gasket will cold

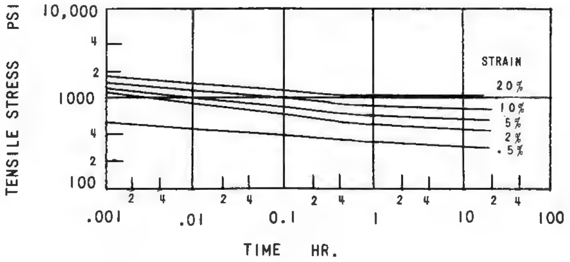


Figure 5

STRESS VS TIME for tensile loading at 73°F.
Tensile stress relaxation under constant strain for molded TFE
(Courtesy of Du Pont and Machine Design)

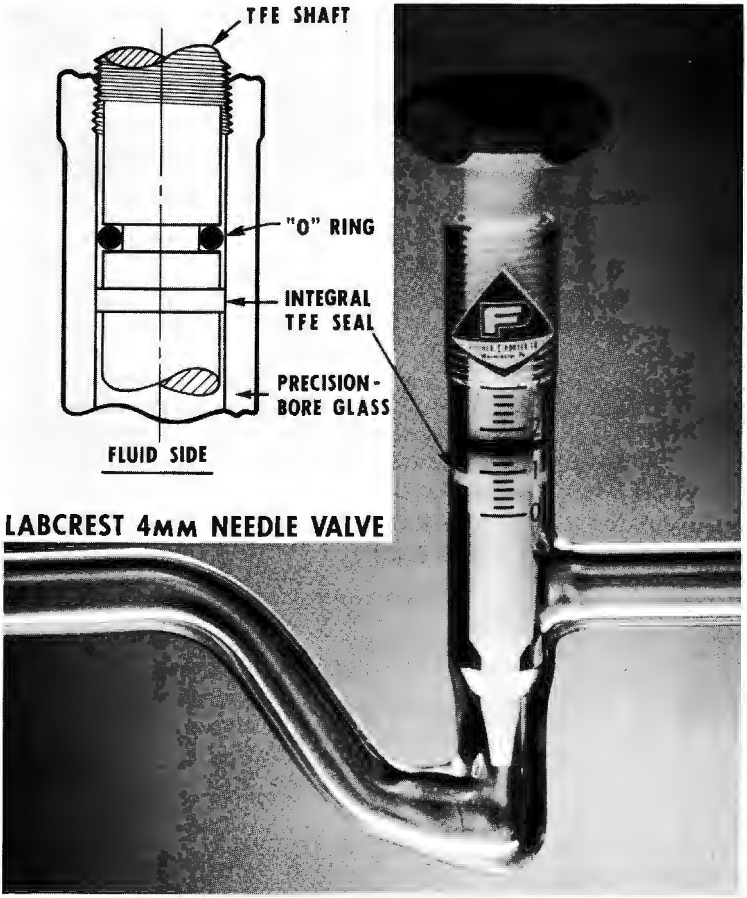


Figure 6

LABCREST 4mm Needle Valve

flow between the flange faces and thus decrease the resultant sealing pressure. Fig. 5 shows tensile stress relaxation curves for unconfined TFE. It can be seen how the tensile stress decays with respect to time under constant strain.

PRODUCT APPLICATIONS OF TFE GLASS DESIGN:

THREADED GLASS VALVES:

The complete line of threaded glass valves manufactured by Fischer and Porter Company is designed to permit only glass and TFE to come in contact with the fluid. From Fig. 6, it can be seen that the 60° valve seat is formed directly into the glass. The TFE stem can then be easily closed against this seat to effect a tight seal. However, leakage around the shaft and past the threads is a more difficult problem to overcome.

The use of a fluorelastomer seal lacks the universal corrosion resistance that is associated with TFE. Conversely, standard TFE "O" rings are not very elastic at room temperature. In order to install the ring, the valve shaft would either have to be made in two sections, or the "O" ring would have to be heated for a shrink fit onto the machined "O" ring groove.

These problems can be avoided by machining an integral ring seal on the valve shaft, and the amount of interference between the glass bore and TFE seal can be initially estimated thru elasticity equations.

The width of the sealing surface should be no larger than .100″. This relatively small surface will permit a very high concentration of bearing stress, without causing objectional valve turning torques. A high turning torque makes it difficult for the user to "feel" shut-off on the 60° valve seat. High resistance to turning may also over-stress the TFE to the point of failure.

Since the sealing surface area is relatively small, let it be assumed that we will create an initial sealing pressure of 1000 PSI, realizing that the TFE will relax under constant strain to some lower stress level. The initial sealing pressure is obtained by making the diameter of the shaft larger than the bore of the glass body.

From the theory of elasticity, the magnitude of the radial interference on the shaft required to produce a given pressure in the mating cylinder is given by:

$$u = \frac{bp}{E_t}[1 - v_t]$$

Where: u = radial displacement of TFE seal after disengagement and assuming perfect elasticity

b = radius of TFE and glass surfaces while in mutual contact, —.1585″

E_t = compressive modulus of TFE—66,500 PSI

v_t = Poisson's ratio of TFE—.46

p = Radial pressure at TFE and glass surface,—1000 PSI

Since the TFE shaft will be forced into the glass shell, the glass strain and resultant stress should be investigated. The glass displacement is given by:

$$u_g \quad - \frac{bp}{E_g\,(c^2 - b^2)}\,[(1 + v_g)c^2 + (1 - v_g)b^2]$$

Where: u_g = radial displacement of the inner surface of the glass

b = radius of TFE and glass surfaces while in mutual contact—.1585″

c = radius of the outer surface of the glass—.240″

E_g = modulus of elasticity of glass—9.1×10^6 PSI

v_g = Poisson's ratio of glass—.20

p = Radial pressure at TFE and glass surface, 1000 PSI

Using an initial pressure of 1000 PSI on the seal of the Fischer and Porter needle valve, and the appropriate elastic constants for TFE and glass, the calculated displacements values are:

u_t = .0013″
u_g = —.000048″

The initial TFE radius will measure $b + u_t$, while the initial glass bore radius will measure $b + u_g$. Substituting a value of .1585″ for b, and converting to diameters we have:

Initial TFE seal diameter = .3196″
Glass precision bore = .3169″

The total interference of the fit is then .0027″. Since we must contend with the usual manufacturing capabilities, the glass bore is held to ± .0002″ I.D., while the TFE seal is held to ± .001″ O.D. Reformation of the glass body is accomplished on a mandrel, which not only provides the required sealing surface accuracy, but also gives us the glass thread and the 60° precision valve seat.

The initial maximum hoop stress developed in the glass body adjacent to the TFE seal, may be calculated from:[6]

Where t_h = hoop stress at glass I.D.

$$t_h = p\,\frac{c^2 + b^2}{c^2 - b^2}$$

Substitution into this equation indicates a tensile hoop stress of 2540 PSI, which would be too high for continuous service. The TFE, however, quickly undergoes stress relaxation, and it is estimated that the stress eventually levels off to about 300 PSI. By way of comparison, the bearing stress on a 2 mm Lab-Crest Stopcock is about 6 PSI if the lock nut is tightened to a normal .6 in-lb torque. The high sealing pressure existing in the needle valve accounts for its superiority in extreme vacuum and pressure applications.

The problem of stress relaxation under constant strain is limited by providing maximum support for the seal. Only .005″ clearance is permitted between the glass bore and main shaft. This will allow the shaft to operate freely up to 250°F., while lending maximum support to the seal.

Since TFE expands at a rate thirty times that of low expansion borosilicate glass, the TFE ring seal will be strained beyond it's elastic limit for continuous temperatures that exceed 160°F. When cycled back to room temperature, only partial compressive recovery will take place, and the result will be leakage. A secondary fluorelastomer seal will take over when the TFE seal becomes ineffective, both in high and low temperature cycling applications. Again, due to the large thermal differences between glass and TFE, the TFE will contract away from the glass at temperatures below 50°F. A regular elastic "O" ring must be provided for these applications. The primary disadvantage of the rubber seal, however, is that it is corrosion prone.

The highest known temperature application for the needle valve has been 400°F. All shaft diameters were reduced to the point where excess straining would not occur at the operating temperature.

There are a number of other design problems relative to the needle valve that are associated with the strength of TFE and glass, and these will be discussed briefly. The diameter of the turning handle must be proportioned to a size that will allow the stem to be seated without overstressing the glass body in tension. Stress concentrations in glass threads cannot be avoided; they can only be distributed by a sufficient number of threads, proper mandrel design, and low torque characteristics for the stem.

The strength of the shaft in torsion must be considered, especially if material is to be removed for an "O" ring groove. If the shaft deflections are too large or the shear stresses are too high with normal closing torques, special "O" rings should be designed with a minimum cross sectional area.

The TFE threads in the Fischer and Porter needle valve are designed with a non-standard pitch diameter in order to reduce backlash. Since one of the design features is precise fluid metering control, it becomes imperative that the stem be finely adjusted for small increments of flow. Backlash in the threads would make accurate flow control difficult to achieve, particularly if the valve is to be calibrated for repeatability.

CHROMATOGRAPHY COLUMNS:

A new line of chromatography columns designed by Fischer and Porter employs only TFE and glass materials for the wetted surfaces. The tooled glass sections are coupled and sealed with a combined TFE and Buna seal. See Fig. 7.

The heavy section of the seal is designed for an interference fit into the glass adaptor. The calculated initial bearing pressure for the seal in the 40 mm column, for example, is 160 PSI. The resultant tensile hoop stress developed at the inner glass wall is 600 PSI. The TFE, however, immediately

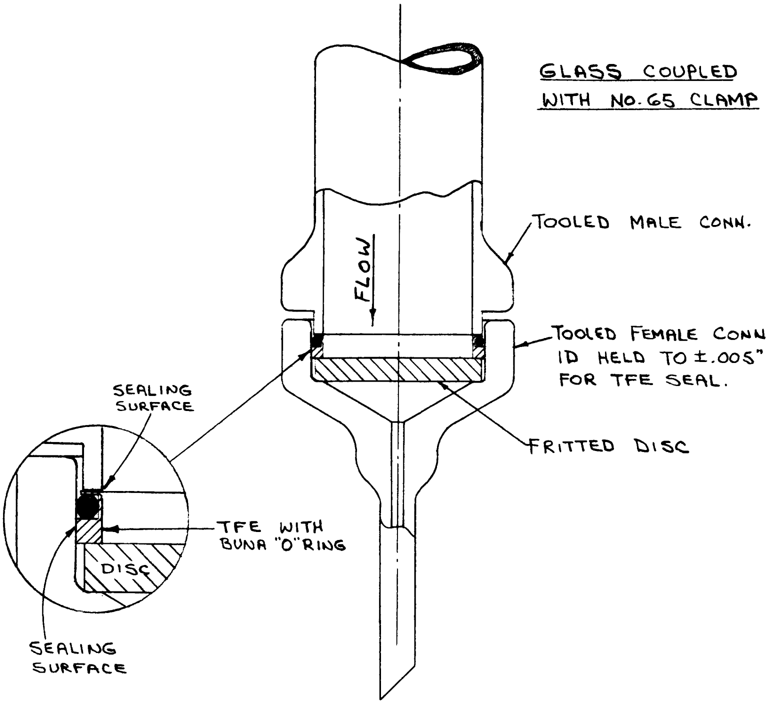


Figure 7
F&P 40mm glass chrome fitting with TFE seal

undergoes stress relaxation, and eventually levels off to some lower constant value. The glass adaptor is hand tooled to a smooth I.D. with a tolerance of ± .005″, ensuring an effective sealing surface. Sealing in this area is independent of the force applied by the pinch clamp.

Securing the tooled male member of the column against leakage is accomplished by combining the elasticity of buna rubber with the inertness of TFE. Since the standard laboratory pinch clamp generates unequal and relatively little closing force, slight misalignment or irregularity in either the male glass or TFE seal will cause leakage thru a solid TFE seal. The insertion of a buna "O" ring, protected from the fluid by a .005″ wall of TFE, will provide the necessary flexibility to the TFE. This design has been successfully used in chromatography, where column pressures generally do not exceed 20 PSIG. Higher pressures are possible with threaded coupling connectors.

REFERENCES

1. Allied Chemical, "Fluorocarbon Plastics", *Materials in Design Engineering,* Manual No. 215, Feb., 1964.
2. Shand, E. B., *Glass Engineering Handbook,* New York, McGraw-Hill, 1958.
3. Wang, Chi-Teh, *Applied Elasticity,* New York, McGraw-Hill, 1953.
4. Gillespie, Saxton, Chapman, "New Design Data for Teflon", *Machine Design,* Jan. 21, 1960, Feb. 18, 1960.
5. Morey, George W., *The Properties of Glass,* New York, Reinhold Publishing Corp., 1938.
6. Billings, J. Harland, *Mechanics and Design of Machines,* Phila., Stephenson Brothers, 1952.

IN ATTENDANCE

The following are on record as having attended the Ninth Symposium on the Art of Glassblowing held at the Sheraton Hotel, Philadephia, Pennsylvania, May 25, 26, 27, 1964. As a fully registered participant, these persons are entitled to a copy of the "Proceedings".

In addition to the names listed herein, 95 persons registered by Day Card, and 63 to attend the Exhibit only.

Airey, Andrew C.	Smith, Kline & French Labs., 1530 Spring Garden St., Phila. 1, Pa.
Alexander, J. Allen	2417 Ritner St., Phila., Pa. 19145
Anderson, Elmer F.	22 Bay State Rd., Natick, Mass.
Anderson, Frederick F.	239 Greenwood Ave., Madison, N. J. 07940
Anderson, Robert H.	R.F.D., Fitzwilliam, N. H.
Armstrong, Gilbert	1017 W. Peterson, Park Ridge, Ill.
Ball, William B.	1116 Ferry Ave., Niagara Falls, N. Y.
Barber, Walter G.	7400 Case Ave., Mentor, Ohio
Barr, W. E.	110 Yorkshire, Pittsburgh, Pa. 15238
Bart, Ray	5815 Stellhorn Rd., Fort Wayne, Ind.
Belz, John F., Jr.	Smith, Kline & French Labs., 1530 Spring Garden St., Phila. 1, Pa.
Benbenek, Jules E.	R.C.A. Labs., Princeton, N. J.
Bennett, Charles A.	Pitman-Dunn Res. & Dev. Lab., Frankford Arsenal, Phila., Pa. 19137
Bergen, George	6218 Dominion Dr., Oxonhill, Md.
Bicknell, E. C.	4161 Andrew St., Petrolia, Ont., Canada
Biermann, Hugo C.	Box 344, Alloway, N. J.
Bivins, John H.	4312 Eighth St., Richmond, Va. 23223
Blankenship, Homer, Jr.	3601 White Oak Dr., Houston, Texas
Blasi, James T.	37 Montvale Ave., Woburn, Mass.
Blomquist, Theodore V.	Rt. 4, Fritztown Rd., Mt. Airy, Md.
Bolan, Theodore W.	11 Maple Ave., Upper Nyack, N. Y.
Brandler, Frank	19 Lincoln Pl., Clifton, N. J.
Brewin, Thomas A.	P. O. Box 24, Burlington, Mass.
Brosious, Edward C.	217 Prospect St., New Haven, Conn.
Burke, Robert	11645 S. W. 62 Ave., Miami, Fla.
Burkett, Fred, Jr.	P. O. Box 91, Millville, N. J.

Burt, Stewart W. . . . . 10 Lewallen Dr., Newport News, Va. 23602

Buttino, Albert L. . . . . Albo Associates, 13 Miles Standish Rd., Schenectady, N. Y. 12306

Cabaniss, Robert H. . . . . 2665 Dove Dr., Florissant, Mo.

Cachaza, Thomas . . . . 1179 Oak Rd., Vineland, N. J.

Camenson, Charles E. . . . . . . 2305 Stone Valley Rd., Alamo, Calif.

Campbell, Clair . . . . 1429 Zettler Rd., Columbus, Ohio 43227

Campbell, W. W., Jr. . . . . 5820 Amelia St., Springfield, Va.

Canning, George . . . . Puerto Rico Nuclear Center, College Station, Mayaguez, P. R. 00709

Capurso, Maurice . . . . 6 Spring St., Medford, Mass.

Carter, Frank B. . . . . 29 Leland Rd., No. Reading, Mass.

Cassidy, C. J. . . . . 430 Greendale Ave., Pittsburgh 18, Pa.

Castle, Frank . . . . 2804 Lehman Pl., Peoria, Ill. 61604

Cavanagh, John R. . . . . R. R. #18, Box 160E, Indianapolis, Ind. 46234

Chaconas, Peter G. . . . . 1408 Buchanan St. N. W., Washington, D. C. 20011

Cheatley, Robert . . . . 3012 Enterprise, Costa Mesa, Calif.

Child, Frank S. . . . . 207 Grant St., Port Jefferson, N. Y. 11777

Child, Ronald K. . . . . 3223 Centennial Dr., Garland, Texas

Christie, Henry L. . . . . 308 Almonte St., Almonte, Ont., Canada

Christopher, James N. . . . . . . 569 Meadow Rd., Somerville, N. J.

Cipolla, John J. . . . . 354 Richmond La., Crystal Lake, Ill. 60014

Circosta, Larry . . . . 215 Aster St., Pittsburgh, Pa. 15235

Conniff, Gerald . . . . ARL, Wright Patterson Air Force Base, Dayton, Ohio

Copeland, Walter P. . . . . 28 Chelten Rd., Havertown, Pa. 19083

Cosgrove, George D. . . . . 2830 Cardenas Dr., N.E., Albuquerque, N. Mex.

Danko, Robert . . . . 350 E. Lake St., Barberton, Ohio

Davis, David A. . . . . 152 E. Main St., Webster, N. Y.

DeCesare, James V. . . . . 3737 Bellaire Blvd., Houston, Texas

Deery, Edward D. . . . . 120 Bennett Ave., New York 33, N. Y.

DeFlorio, William J. . . . . Robbins Dr., Carlisle, Mass.

DeLeonibus, Enrico . . . . 5906 Rosedale Dr., Hyattsville, Md.

Delly, John G. . . . . 5544 W. Cortland St., Chicago, Ill. 60639

DeMaria, Vincent C. . . . . Mt. Hope Rd., Rockaway, N. J.

Deminet, Czeslaw . . . . Boeing Scientific Res. Labs., P. O. Box 3981, Seattle, Wash. 98124

DeWolff, William N. . . . . The Upjohn Co., Kalamazoo, Mich. 49001

Dolenga, Arthur . . . . 44045 Donley Dr., Utica, Mich. 48087

Domizio, Arthur . . . . 44 Nichols Ave., Yonkers, N. Y.

Doody, Thomas J. . . . . 319 S. Cass, Westmont, Ill.

Dorsi, David C. . . . . 240 Morris St., Stirling, N. J.

Drechsel, Helmut E. . . . . Churchville, Pa. 18966

Dusek, Leo F. . . . . 3425 Grantwood Dr., Cleveland, Ohio 44134

Dymock, George . . . . 153 Atlas Ave., Toronto, Ont., Canada

Eckberg, Edwin E. . . . . Ecklux Vacuum Lab., P. O. Box 331, Bedford, Mass.

Engelman, Charles T., Jr. . . . . The Fredericks Co., Philmont Ave., Bethayres, Pa.

Epperson, Howard L. . . . . 124 Cherokee Ave., Athens, Ga. 30601

Falconer, Dennis G. . . . . 41 Oak St., Bairdford, Pa. 15006

Faust, Gerald . . . . P. O. Box 97, Exton, Pa.

Federline, C. D. . . . . 1176 Sharp Rd., Vineland, N. J. 08360

Finkenbeiner, G. . . . . 23 Alaska Ave., Bedford, Mass.

Fischer, Harold E. . . . . 1917 Smyers Dr., Benton Harbor, Mich. 49022

Forgnoni, Robert . . . . 53 Glenn Terr., Vineland, N. J.

Fox, Joseph J. . . . . 747 Monroe St., Rockville, Md.

French, J. L. A. . . . . Chem. Dept., Univ. of Toronto, Toronto 5, Ont., Can.

Galfano, Sam J. . . . . 2800 Fremont St., Rolling Meadows, Ill.

Garner, T. H. . . . . Garner Glass Co., 177 So. Indian Hill Blvd., Claremont, Calif.

Geyer, Hans E. . . . . 13 Cedarwood Dr., Huntington Sta., L. I., N. Y.

Geza, Dombi . . . . 2980 E. Euclid, Apt. 4, Boulder, Colo. 80302

Gilhooley, William A. . . . . . . 1466 VanCurler Ave., Schenectady, N. Y.

Glover, John A. . . . . Sinclair Research Co., 400 E. Sibley Blvd., Harvey, Ill.

Godown, Vernon D. . . . . Turk Rd., Warrington, Pa.

Goldman, David . . . . 56-37 220th St., Bayside 64, N. Y.

Gorham, Jack . . . . Columbia Univ., 538 W. 120 St., New York N. Y.

Gray, Lou ....227 Ridgely Dr., Verona, Pa.
Green, Harry F.............2255 Stone Valley Rd., Alamo, Calif.
Greenwood, Ralph M.......1558 So. Rogers, Bartlesville, Okla.
Greer, Robert ....334 Melwood Ave., Pittsburgh 13, Pa.
Gross, Russell ....111 W. Mill, Wauconda, Ill.
Gunther, Adolf P............85-85 98th St., Woodhaven 21, N. Y.
Gutilla, Sam J. ....5905 N. Mobile, Chicago, Ill.
Hagedorn, James A. ....5946 Glenwood Ave., Chicago, Ill. 60626
Hager, Adolph G............2311 Dorsett Dock Rd., Pt. Pleasant, N. J. 08743
Hahn, George ....Woodland Ave. Mach. Co., Inc., 901-11 Woodland Ave., Sharon Hill, Pa.
Hamarlow, John ....2249 Tohickon La., Neshaminy, Pa.
Hapstack, Richard J.........212 Marcella Rd., Parsippany, N. J. 07054
Hawkins, A. J...............P. O. Box 541, Alfred, N. Y. 14802
Hayes, Frank L. ....2233 S. Clinton, Berwyn, Ill. 60402
Hegedus, Charles ....930 Sargent St., Whittier, Calif.
Henson, Thomas A..........Physics Dept., Duke Univ., Durham, N. C.
Hernandez, Peter ....1327 Dorchester Ave., Ottawa 3, Ont., Canada
Heyn, Carl ....217 Dodge Ave., Corning, N. Y.
Heyn, Hermann A. ....607 Buena Loma St., Altadena, Calif.
Hiergesell, Valentine ....1067 Holly Tree Rd., Abington, Pa.
Higgins, Columb G..........1875 Purdue La., Maple Glen, Pa.
Hodyno, Walter ....91-35 193 St., Hollis, N. Y.
Holle, Robert ....1947 Bremerton, Cleveland 24, Ohio
Horn, Francis ....215 E. 5th Ave., Conshohocken, Pa.
Howell, Leigh B............121 Santa Paula Ave., Santa Barbara, Calif.
Hunter, Morgan P., Jr......46 E. Ann Rd., Broomall, Pa.
Huth, Harry J. ....9859 Ione La., St. Louis, Mo. 63123
Hydro, George ....715 W. Olive St., Corona, Calif.
Ingram, B. L...............Box 900, Dallas, Texas
Johnson, Victor L. ....238 Mimosa Dr., Centerville, Ohio 45459
Johnson, Walter, Jr.........P. O. Box 568, Millville, N. J.
Jonson, Jacob ....7050—43 Ave. N. E., Seattle, Wash. 98115
Jubera, A. M. ....Mellon Inst., 4400—5th Ave., Pittsburgh, Pa.

Kane, Thomas J. . . . . 114 Clendenny Ave., Jersey City, N. J.

Kay, Peter L. . . . . 1142 S. Highland, Arlington Hgts., Ill.

Kennedy, Frederick G. . . . . . Texas Instruments Inc., P. O. Box 5474, Dallas, Texas 75222

Kervitsky, Joseph . . . . 308 Virginia Hills Ave., Alexandria, Va.

Kessler, Gunther . . . . 903 Rose Ave., Ann Arbor, Mich.

Klebanoff, Joseph . . . . 7600 Atwood St., Dist. Hgts., Md.

Klein, Edwin I. . . . . 8804 Reading Rd., Silver Spring, Md.

Kleinert, Richard A. . . . . 12811 Sioux Ave., Detroit 39, Mich.

Knisely, Samuel . . . . 72 N. Main St., Mullica Hill, N. J. 08062

Koch, Edward . . . . 28 Polhemus Terr., Whippany, N. J.

Koch, Stanley J. . . . . 626 Schuyler Ave., Kearny, N. J. 07032

Kocsi, Andrew . . . . 32 Holly Pl., Edison, N. J.

Kramer, Harold C. . . . . 53 Fox Hedge Rd., Saddle River, N. J.

Kuenstner, George F. . . . . 332 Cottman St., Cheltenham, Pa. 19012

Kummer, H. A. . . . . 40 E. 89th St., New York, N. Y.

Laderoute, A. G. . . . . 13 Brooklane Rd., Southington, Conn.

Lamb, Thomas H. . . . . 1826 Sherwood St. Allentown, Pa.

Last, Homer C. S. . . . . National Research Council, Div. of Applied Chem., Montreal Rd., Ottawa, Ont., Canada

Lawrence, William I. . . . . 1909 Crescent Dr., Champaign, Ill.

Lees, John . . . . Dept. of Physics, Univ. of British Columbia, Vancouver 8, B. C., Canada

Lejeune, John P. . . . . 2344 Beaton Way, Orange, Calif.

Lenzi, David J. . . . . 416 Sycamore St., Elizabethtown, Ky. 42701

LeRoy, Arlen B. . . . . 156 Main St., Bridgeport, Conn.

Leue, Jim . . . . 7500 Brill Rd., Cincinnati 43, Ohio

Leuthner, H. . . . . Vactronic Res. Labs., 198-10 32nd Ave., Flushing 58, N. Y.

Lewis, Chester J. . . . . 35 Spackenkill Rd., Poughkeepsie, N. Y. 12603

Liebson, Morris . . . . 2851 Larkspur St., Yorktown Hgts., N. Y.

Liedtke, Arnold . . . . 617 Wavery Dr., Benton Harbor, Mich. 49022

Lillie, Don . . . . 432 Oakdale Dr., Smyrna, Ga. 30080

Lindsay, T. Duncan . . . . 5420 Thorndale Rd., Calgary, Alta., Canada

Litton, Charles V. . . . . P. O. Box 949, Grass Valley, Calif. 95945

Litz, Charles M. ....400 Avery Ct., Joppatowne, Md. 21085

Lockwood, Melvyn ....550 N. Fairoaks Ave., Sunnyvale, Calif.

Logiudice, John ....5356 N. Pioneer, Chicago, Ill.

Lord, Edward E. ....58 Cardinal Rd., Levittown, Pa.

Lorimer, Robert ....837 Mulberry La., Sunnyvale, Calif.

Luisi, Joe ....836 Park Ave., Vineland, N. J.

Lutter, Eugene ....Granville-Phillips, Box 1290, Boulder, Colo. 80301

Machek, Elco ....228 E. 80 St., New York, N. Y. 10021

Mack, Arthur D. ....Chem. Dept., Catholic Univ., Washington 17, D. C.

Macur, Mike ....97 Glover Ave., Yonkers, N. Y.

Mahler, Hermann ....2028 Baker Ave., Schenectady, N. Y. 12309

Maiolatesi, Elmo ....35 Henry Ave., Baltimore 36, Md.

Malloy, F. J. ....1171 Harvard Rd., Pitcairn, Pa. 15140

Mason, Austin ....6015 Milne Blvd., New Orleans, La. 70124

Mattison, Lester H. ....Texas Instruments Inc., 13500 N. Central Expressway, Dallas, Texas

Merriam, Donald R. ....6990 Haines St., Cincinnati, Ohio 45227

Messick, George E. ....370 Papermill Rd., Newark, Del.

Meyer, Frank ....Garretson Ave., Islip, N. Y.

Meyer, I. A. ....Box 318, Wading River, N. Y.

Mezynski, Stanley ....Physics Dept., North Carolina State Univ., Raleigh, N. C.

Mittelman, Richard ....114 Wentworth Dr., Radnor Woods, Claymont, Del.

Moran, J. J. ....Landis Ave. & Spring Rd., Vineland, N. J. 08360

Morphet, Keith D. ....6211 Springhill Dr., Greenbelt, Md. 20770

Morris, James F. ....716 Clinton, Evanston, Ill. 60201

Myers, Dave ....3687 Weber Rd., Saline, Mich.

McCaffrey, Wm. A. ....18 Walnut Rd., Vineland, N. J.

McKelvey, Thos. J. ....Smith, Kline & French Labs., 1530 Spring Garden St., Phila. 1, Pa.

McKisick, Robert ....P. O. Box 1201, Boulder, Colo.

McNear, M. F. ....113 Lancaster Terrace, Hampton, Va. 23366

Nazzewski, Matthew ....Sprague Electric Co., Marshall St., No. Adams, Mass.

Newcomb, Howard R. ......710 Mulberry St., Millville, N. J.

Nilsson, Per	2245 S. W. 28 St., Miami, Fla. 33133
Nocero, Joseph	212 Columbia Ave., Horsham, Pa.
O'Brien, Donald M.	R.F.D. #1, Hudson, N. H.
Oster, Harold F.	Geier & Bluhm, Inc., 594 River St., Troy, N. Y.
Osty, Sigmund J.	8404 Keystone Ave., Skokie, Ill.
Otto, Manfred R.	2821 Maplewood St., Ann Arbor, Mich.
Page, J. A. L.	787 Chapman Blvd., Ottawa, Ont., Canada
Palazzolo, Joseph	8416 Robindale, Dearborn Hgts. 6, Mich.
Panczner, J. E.	1507 Hagley Rd., Toledo, Ohio
Panczner, W. J.	1424 Barbara Ave., Clearwater, Fla. 33515
Parks, George E.	29 Buck Run La., Malvern, Pa.
Podbielniak, Walter J.	850 N. Lake Shore Dr., Chicago 11, Ill.
Pollock, James J.	1002 E. Sugnet, Midland, Mich.
Poole, R. W.	100 Cedar La., Oak Ridge, Tenn.
Prost, Saul M.	P. O. Box 51, Malden, Mass.
Putnam, Carl	3011 Main St., Glastonbury, Conn. 06033
Rak, Steve	Chem. Dept., Univ. of British Columbia, Vancouver 8, Canada
Reinhardt, Karl	E. R. Squibb & Sons, Georges Rd., New Brunswick, N. J.
Roensch, Arno P.	533 Myrtle St., Los Alamos, N. Mex.
Rothfels, John	10 Valdez, Dugway, Utah
Rovey, John S.	P. O. Box 666, Woodbury, N. J.
Ryall, Allan R.	1567 Nuthatch La., Sunnyvale, Calif.
Ryan, Lawrence W.	Ryan, Velluto & Anderson, Inc., 103 First St., Cambridge, Mass.
Safferling, Ottmar A.	97-18 77 St., Ozone Park, N. Y. 11416
Sales, Wm.	H. S. Martin Co., 1916 Greenleaf, Evanston, Ill.
Saoner, Joseph L.	599 North Valley Ave., Vineland, N. J.
Sarfi, George	1795 Baseline, Ottawa, Ont., Canada
Saydek, Michael C.	234 Richards Ave., New Market, N. J.
Schaefer, Fred	The Machlett Labs., Inc., 1063 Hope St., Springdale, Conn. 06879
Schipmann, Robert	12 Kendall Rd., Kendall Park, N. J. 08824
Schmauder, Johnnie	10255 Beaverton Hillsdale Hwy., Beaverton, Ore.

Schneider, W. O.	46 Kathleen Dr. E., Syosset, L. I., N. Y.
Schreiber, Aldo S.	2155 W. Arthur Ave., Chicago, Ill. 60645
Schumann, Karl	299 Riverdale Dr., Fort Lee, N. J.
Searle, R. H.	3102 Santee Ave., Aiken, S. C. 29801
Shanks, Ralph J.	House of Glass, 34074 Harper Ave., Mt. Clemens, Mich. 48043
Shanks, Virginia A.	House of Glass, 34074 Harper Ave., Mt. Clemens, Mich. 48043
Shedd, Fred J.	3800 Mt. Read Blvd., Rochester, N. Y. 14616
Shipley, D. L.	2915 Lincoln Ave., Parma, Ohio 44130
Shotts, E. F.	The Goodyear Tire & Rubber Co., 142 Goodyear Blvd., Akron, Ohio 44316
Simon, Richard H.	1541 Deane Blvd., Racine, Wis.
Sites, George A.	Houdry Process & Chem. Co., Div. of Air Products & Chems., Inc., P. O. Box 427, Marcus Hook, Pa. 19061
Slominski, Harry J.	P. O. Box 65, Tarrytown, N. Y.
Smart, David R.	P. Lorillard Co., 2525 East Market St., Greensboro, N. C.
Smith, John L., Jr.	Andrews Glass Co., Vineland, N. J.
Smith, M. Howe	2142 Herblew Rd., Warrington, Pa.
Smith, W. C.	Houghton Park Lab., Corning Glass Works, Corning, N. Y.
Smulders, J.	Dept. of Elec. Eng., Univ. of Minnesota, Minneapolis, Minn. 55455
Snidow, R. D.	1708 Glorietta N.E., Albuquerque, N. Mex.
Snyder, Carl R.	19 Duane Rd., Edison, Pa.
Snyder, Dale	2974 W. Stewart, R. #7, Midland, Mich.
Souza, Raymond L.	59 Mishawum Rd., Woburn, Mass.
Spessard, Lewis C.	4604 Hummer Rd., Annandale, Va. 22003
Squeo, Guy J.	5270 N. Lind Ave., Chicago, Ill. 60630
Staiger, Al	200-06 28 Ave., Bayside, N. Y.
Stanley, Russell	Stanley Scientific Glass, Inc., Box 400, Tullytown, Pa.
Stevens, Ralph	Harrison Rd., No. Branford, Conn.
Stiplosek, Martin	M & M Glassblowing Lab. Inc., 811 N. Prairie Ave., Hawthorne, Calif.
Strasburger, Robert R.	2209 A Ernest Ave., Redondo Beach, Calif.

Sward, John .... P. O. Box 89, Plainfield, Pa.

Tarczynski, J. .... 45 Hazelwood Ave., Livingston, N. J.

Thompson, A. Robert .... 9525 Evans St., Phila., Pa. 19115

Thornton, Mrs. Helen V. ... 14 Taylor Rd., Conshohocken, Pa. 19428

Trechel, Eugene J. .... Pine Brook Rd., Towaco, N. J.

Turner, Thomas A. .... East Holden, Maine

Unger, George W. .... 3189—5th St., Boulder, Colo. 80302

Upton, Lee O. .... American Optical Co., 14 Mechanic St.,
Southbridge, Mass.

Uthman, Paul W. .... R.D. 1, Evans City, Pa.

van Hespen, C. C. .... 1443 East 83 St., Chicago, Ill. 60619

Velluto, Anthony J., Sr. .... 66 Russett Lane, Melrose, Mass.

Voyer, L. A. .... 9 Knollwood Circle, Weymouth, Mass.

Wagner, Betty .... 24 Sycamore Rd., Levittown, Pa.

Walrod, Alfred H. .... 70 Alviso St., Santa Clara, Calif.

Walther, Karl .... Miller Place Rd., Middle Island, L. I.,
N. Y.

Weiss, Ferdinand M. .... 112 Wayne Dr., Riverton, N. J.

Weiss, Gunther .... 2025 S. W. Briggs Ct., Beaverton, Ore.

West, Joseph .... 908—87th St., Niagara Falls, N. Y.

Whittemore, Francis D. ..... 480 Wade Ave., Lansdale, Pa.

Wilson, Robert R. .... 6426 Mona Lisa Ct., Cincinnati, Ohio 45239

Wilt, Wm. A. .... Wilt Lab. Glass Blowing, Inc., 860 Albany-
Shaker Rd., Latham, N. Y

Winkler, Lyle D. .... 708 E. Liberty St., Wauconda, Ill.

Wolfe, Alfred M. .... P. O. Box 252, Indian Orchard, Mass 01051

Woods, Richard M. .... 280 Morrissey St., Pittsburgh, Pa. 15214

Wright, Gerald A. .... Lancaster Glass Corp., 220-226 W. Main St.,
Lancaster, Ohio 43130

Young, Robert D. .... 42 Whittier Blvd., Poughkeepsie, N. Y.
12603

Zidlick, William .... 370 West Ave., Norwalk, Conn.

Zurek, Tony A. .... 504 S. Dixon Ave., Cary, N. C. 27511

Zwirblis, Henry G. .... 17 Lillian Rd., Nesconset, L. I., N. Y.

Zwirblis, Stanley .... 19 Holly Rd., Lake Ronkonkoma, N. Y.

REGISTRATION—NON-MEMBERS

Albertson, Ralph .... 320 Grant Ave., Pitman, N. J.
Anderberg, Dane .... Lawrence Radiation Lab., Berkeley, Calif.
Bhandarkar, Shridhar G. .... 734 Middle Ave., Menlo Park, Calif.
Bishop, James H. .... 72 Florence St., Columbus 4, Ohio
Borodatschew, Wassily ..... 868 Wake Forest Rd., Dayton 31, Ohio
Brady, Don .... 12301 S. 70th Ave., Palos Hgts., Ill.
Brusselers, C. .... 5711—114A St., Edmonton, Canada
Cipperly, Arnold C. .... 8 Wendell Ave., Troy, N. Y.
Crigler, Alfred .... 2801 Cortland Pl., Washington, D. C.
Cummins, Robert K. .... Willoughby Quartz Plant, General Electric Co., Campbell Rd., Willoughby, Ohio 44094
Curtis, D. .... Quickfit & Quartz Ltd., Tilling Dr., Stone, Staffordshire, England
Dawson, John T. .... 113 Warwick Ave., Cinnaminson, N. J.
Earley, K. D. .... 216-05—48 Ave., Bayside, N. Y.
Ensell, George .... 14 Braemar, Ottawa, Canada
Erich, James S. .... R. D. #1, Zionsville, Pa. 18092
Evans, B. .... National Research Council, Sussex St., Ottawa, Ont., Canada
Franer, William L. .... Monsanto Res. Corp., Mound Lab., Miamisburg, Ohio
Gass, George .... 44 Mountain Rd., Rockaway, N. J.
Goodyear, Leon F. .... 705 W. Vermont, Urbana, Ill.
Grigassy, Gene .... 5806 Ardmore, Houston, Texas 77021
Grohe, Edward .... 118 Willow Ave., New Brunswick, N. J.
Hamon, Richard .... 7368—7th N., Liverpool, N. Y.
Holland, J. R. .... Hickory Lane, Corning, N. Y.
Jackson, Edmund J. .... 5021 Bradley Blvd., Bethesda, Md.
Kalbin, Alex J. .... 219 Hutton St., Gaithersburg, Md.
Keagle, Fred .... 137 Cutler Ave., Corning, N. Y.
Klees, Randall .... 164 E. 2nd St., Lansdale, Pa. 19466
Koffen, Allan H., Jr. .... 111 W. Mill St., Wauconda, Ill. 60084
Kristof, Egon M. .... Postae St. "B", Box 583, Ottawa, Ont., Canada
Kump, William R. .... National Institutes of Health, Bethesda, Md.

Maiolatesi, F. ....302 Stemmers Run Rd., Baltimore, Md.

Morse, William ....Bell Telephone Labs., Union Blvd., Allentown, Pa.

Murphy, Alonzo C. ....110 W. Aaron Dr., State College, Pa. 16801

Murphy, E. James ....2015 Crestland Dr., Ann Arbor, Mich. 48104

Nelson, Lawrence W. ....Abbott Rd., Brattleboro, Vt. 05301

O'Brien, Kenneth E. ....E. I. du Pont de Nemours & Co., Inc., Jackson Lab., P. O. Box 525, Wilmington, Del. 19899

O'Brien, Thomas M. ....2211 Story Ave., Schenectady, N. Y. 12309

Omiecinski, Sigmund ....10545 Wabash Ave., Chicago 28, Ill.

Pelton, Charles H. ....300 Willow St., State College, Pa.

Potter, Elmer F. ....R. D. #3, Corning, N. Y.

Ray, James D. ....287 Curtis Dr., Wilmington, Ohio

Schrickel, Emil O. ....227 Dodge Ave., Corning, N. Y.

Seitz, Thomas E. ....2158 W. 67 St., Cleveland, Ohio 44102

Sitko, Joseph J. ....Imperial Arms, Lansdale, Pa.

Snyder, Charles ....344 Elmwood Dr., Naperville, Ill.

Soehn, Richard ....Date Reagents Inc., 1851 Delaware Pkwy., Miami, Fla.

Stang, Richard C. ....10 Chandler St., Rockledge, Pa.

Sullivan, Frank P. ....P. O. Box 73, Lexington, Mass.

Taylor, Roger K. ....3122 N. Calvert St., Baltimore, Md. 21218

Valpey, Theodore S., Jr. ....1244 Highland St., Holliston, Mass.

Wade, Robert E. ....338 Arms Dr., Fairborn, Ohio

Warren, Thomas S. ....Ultra-Violet Products, Inc., 5114 Walnut Grove, San Gabriel, Calif. 91778

Weppener, Richard T. ......908 Alpine Ave. #6, Boulder, Colo. 80302

Welzel, Otto ....110 W. First St., Corning, N. Y.

Whitehead, J. A. ....223 Kendall Rd., Kendall Park, N. J.

Wolff, Hans ....H. S. Martin & Son, 1916 Greenleaf, Evanston, Ill.

Yeager, Paul V. ....414 "J", Chula Vista, Calif.

Zagorac, Joseph ....7520 Calumet St., Pittsburgh 18, Pa.

REGISTRATION—NON-MEMBERS

Albertson, Ralph .... 320 Grant Ave., Pitman, N. J.

Anderberg, Dane .... Lawrence Radiation Lab., Berkeley, Calif.

Bhandarkar, Shridhar G. .... 734 Middle Ave., Menlo Park, Calif.

Bishop, James H. .... 72 Florence St., Columbus 4, Ohio

Borodatschew, Wassily ..... 868 Wake Forest Rd., Dayton 31, Ohio

Brady, Don .... 12301 S. 70th Ave., Palos Hgts., Ill.

Brusselers, C. .... 5711—114A St., Edmonton, Canada

Cipperly, Arnold C. .... 8 Wendell Ave., Troy, N. Y.

Crigler, Alfred .... 2801 Cortland Pl., Washington, D. C.

Cummins, Robert K. .... Willoughby Quartz Plant, General Electric Co., Campbell Rd., Willoughby, Ohio 44094

Curtis, D. .... Quickfit & Quartz Ltd., Tilling Dr., Stone, Staffordshire, England

Dawson, John T. .... 113 Warwick Ave., Cinnaminson, N. J.

Earley, K. D. .... 216-05—48 Ave., Bayside, N. Y.

Ensell, George .... 14 Braemar, Ottawa, Canada

Erich, James S. .... R. D. #1, Zionsville, Pa. 18092

Evans, B. .... National Research Council, Sussex St., Ottawa, Ont., Canada

Franer, William L. .... Monsanto Res. Corp., Mound Lab., Miamisburg, Ohio

Gass, George .... 44 Mountain Rd., Rockaway, N. J.

Goodyear, Leon F. .... 705 W. Vermont, Urbana, Ill.

Grigassy, Gene .... 5806 Ardmore, Houston, Texas 77021

Grohe, Edward .... 118 Willow Ave., New Brunswick, N. J.

Hamon, Richard .... 7368—7th N., Liverpool, N. Y.

Holland, J. R. .... Hickory Lane, Corning, N. Y.

Jackson, Edmund J. .... 5021 Bradley Blvd., Bethesda, Md.

Kalbin, Alex J. .... 219 Hutton St., Gaithersburg, Md.

Keagle, Fred .... 137 Cutler Ave., Corning, N. Y.

Klees, Randall .... 164 E. 2nd St., Lansdale, Pa. 19466

Koffen, Allan H., Jr. .... 111 W. Mill St., Wauconda, Ill. 60084

Kristof, Egon M. .... Postae St. "B", Box 583, Ottawa, Ont., Canada

Kump, William R. .... National Institutes of Health, Bethesda, Md.

Maiolatesi, F. . . . . 302 Stemmers Run Rd., Baltimore, Md.

Morse, William . . . . Bell Telephone Labs., Union Blvd., Allentown, Pa.

Murphy, Alonzo C. . . . . 110 W. Aaron Dr., State College, Pa. 16801

Murphy, E. James . . . . 2015 Crestland Dr., Ann Arbor, Mich. 48104

Nelson, Lawrence W. . . . . Abbott Rd., Brattleboro, Vt. 05301

O'Brien, Kenneth E. . . . . E. I. du Pont de Nemours & Co., Inc., Jackson Lab., P. O. Box 525, Wilmington, Del. 19899

O'Brien, Thomas M. . . . . 2211 Story Ave., Schenectady, N. Y. 12309

Omiecinski, Sigmund . . . . 10545 Wabash Ave., Chicago 28, Ill.

Pelton, Charles H. . . . . 300 Willow St., State College, Pa.

Potter, Elmer F. . . . . R. D. #3, Corning, N. Y.

Ray, James D. . . . . 287 Curtis Dr., Wilmington, Ohio

Schrickel, Emil O. . . . . 227 Dodge Ave., Corning, N. Y.

Seitz, Thomas E. . . . . 2158 W. 67 St., Cleveland, Ohio 44102

Sitko, Joseph J. . . . . Imperial Arms, Lansdale, Pa.

Snyder, Charles . . . . 344 Elmwood Dr., Naperville, Ill.

Soehn, Richard . . . . Date Reagents Inc., 1851 Delaware Pkwy., Miami, Fla.

Stang, Richard C. . . . . 10 Chandler St., Rockledge, Pa.

Sullivan, Frank P. . . . . P. O. Box 73, Lexington, Mass.

Taylor, Roger K. . . . . 3122 N. Calvert St., Baltimore, Md. 21218

Valpey, Theodore S., Jr. . . . . 1244 Highland St., Holliston, Mass.

Wade, Robert E. . . . . 338 Arms Dr., Fairborn, Ohio

Warren, Thomas S. . . . . Ultra-Violet Products, Inc., 5114 Walnut Grove, San Gabriel, Calif. 91778

Weppener, Richard T. . . . . . . 908 Alpine Ave. #6, Boulder, Colo. 80302

Welzel, Otto . . . . 110 W. First St., Corning, N. Y.

Whitehead, J. A. . . . . 223 Kendall Rd., Kendall Park, N. J.

Wolff, Hans . . . . H. S. Martin & Son, 1916 Greenleaf, Evanston, Ill.

Yeager, Paul V. . . . . 414 "J", Chula Vista, Calif.

Zagorac, Joseph . . . . 7520 Calumet St., Pittsburgh 18, Pa.